EniVal: a tool for assessing the relative environmental impact of continuous chemical processes

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ENIVAL

A TOOL FOR ASSESSING THE RELATIVE ENVIRONMENTAL IMPACT OF CONTINUOUS CHEMICAL PROCESSES

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Summary

This thesis presents the development and use of EniVal (Environmental Impact Valuation). EniVal is an environmental impact assessment tool for use in the design of continuously operating chemical processes. EniVal calculates an overall impact score for the process by combining a set of scoring systems for the determination of the impact of each pollutant released, with discharge data from the process. The impact scores are based on selected parameters which are indicative of environmental impact. These impact scores are combined with discharge data based on quantities rather than the more traditional use of environmental concentrations. The design of EniVal is based on a tree structure with two main branches considering both the long-term and short-term environmental impacts of processes.

For ease of use, EniVal has been implemented as a computer-based process engineering tool. It operates as an executable Windows™ application which enables clear and simple representation of all stages of the analysis. EniVal is a tool that can be used for selecting the Best Environmental Option (BEO) for new processes and also in the redesign of existing plants in order to meet increasingly stringent discharge limits.

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A	Atmospheric discharge
ACID	Acidification score
ACTS	Advisory Committee on Toxic Substances
AU	Atom Utilisation
BAT	Best Available Techniques
BATNEEC	Best Available Techniques Not Entailing Excessive Cost
BC	Bioconcentration score
BCF	Bioconcentration factor
BOD	Biochemical oxygen demand
BPEO	Best Practicable Environmental Option
c	concentration
CFC	Chlorofluourcarbons
CO	Carbon monoxide
COPA	Control Of Pollution Act
ΔHc	Heat of combustion
d	soil density
DAM	Damage score
DDT	Common insecticide with formula: Cl(C6H4)CHCCl3(C6H4)Cl
DEG	Degradation score
DEOX	Deoxygenation score
DISP	Dispersion score
DO	Dissolved oxygen concentration
EAL	Environmental Assessment Level
EC	European Community
EC50	Ecotoxicity
ECO	ECOlogical scarcity method
EIA	Environmental Impact Assessment
EIS	Environmental Impact Statement
ELF	Environmental Load Factor
EniVal	Environmental Impact Valuator
ENVOP	ENVironmental OPtimisation
EPA	Environment Protection Act 1990

EPS	Environmental Priority Strategies
EQS	Environmental Quality Standard
ET	Environmental Theme method
ETP	On-site effluent treatment plant
EXPL	Explosivity score
FEI	Fire and Explosion Index
Fi	Fraction of pollutant in medium I
FLAM	Flammability score
fo.c.	fraction of organic carbon in soil
GMB	Graphical Mass Balance
GW	Global Warming score
GWP	Global Warming Potential
HAZ	Hazard score
HMIP	Her Majesty's Inspectorate of Pollution
I	Impact
I.E.I.	Integrated Environmental Index
IPC	Integrated Pollution Control
IRIS	Integrated Risk Information System
Koc	soil adsorption constant
Kow	noctanol-water partition coefficient
Kw	Air-water partition coefficient
L	Land discharge
LAND	Land reuse score
LC50	Concentration required for 50% population death
LD50	Dose required for 50% population death
LOC	Location factor
LT	Long-term
MAQI	Mitre Air Quality Index
MEL	Maximum Exposure Limit
MEN	Mass Exchange Networks
MF	Material Factor
MOD	Modification score
MSDS	Material Safety Data Sheets
MW	Molecular weight

MWSc	Molecular weight score
MWth	MW thermal (energy rating)
NAAQS	National Ambient Air Quality Standards
NO3-	Nitrate ion
Novem	Netherlands Agency for Energy and the Environment
NOx	Nitrogen oxides
NRA	National Rivers Authority
O3	Ozone
OC	Ozone creation score
OEL	Occupational Exposure Limit
OES	Occupational Exposure Standard
OSD	Off-site disposal
OX	Oxidants
PAH	Polyaromatic hydrocarbons
PC	Personal Computer
PEC	Predicted environmental concentration
PERS	Persistence score
PNEC	Predicted no-effect concentration
PO4	Phosphates
POCP	Photochemical Ozone Creation Potential
Qi	Quantity of pollutant I discharged
QT	Process production level
RfD	Reference Dose (carcinogenicity)
RIVM	Netherlands National Institute of Public Health and Environmental Protection
S	Solubility
SOL	Solubility score
SOx	Sulphur oxides
ST	Short-term
STAB	Atmospheric stability parameter
TOPO	Local topography parameter
TOX	Toxicity score
TOXCHRON	Chronic toxicity
tpa	Tonnes per annum

TSP	Total suspended particulates
UK	United Kingdom
UOD	Ultimate Oxygen Demand
US EPA	United States Environment Protection Agency
V	Volume
VOC	Volatile organic compounds
W	Water discharge
WATCH	Working group on the Assessment of Toxic CHemicals
WQIAU	Unweighted Arithmetic Water Quality Index
wt%	Weight per cent

Chapter 1

Introduction

In recent years, due to increasing restrictions being placed on the levels of pollutants being released to the environment from chemical industries there has been much debate about the need to progress towards the 'zero discharge process'. While the concept of a 'zero discharge process' may be more idealistic than realistic, moves are being made to reduce significantly the impact that chemical processes have on the environment.

1.1 The history of environmental concerns

Over the last three decades the degradation of the environment caused by human activity has been one of the major issues of global concern to governments, industry and the general public. During this period the public gradually became aware of the impact that chemical processes had on their lives. In response to this there has been a succession of legislation introduced in the EC and the UK in order to control and deal with the problem of waste production.

The Clean Air Act was originally introduced in the UK in 1956 in order to protect the environment from smoke, dust and fumes. It was then modified in 1968 and again in 1993. The original act was one of the first attempts to control the effects of industrial processes on the environment. The emission of dark smoke from any chimney was prohibited and the rule was enforced strictly by the local authorities. As the legislation changed the authorities became more proactive by requiring all combustion processes of greater than a defined limit to burn smokeless fuels. The operators of the processes were required to notify the relevant local authority before the process could be built.

In 1985 the EC became a signatory to the Montreal Protocol as part of the Vienna Convention which introduced control measures to ensure the protection of the ozone layer by restricting the use of chlorofluorocarbons (CFCs) and halons. At the Second World Climate Conference in 1990 the EC agreed to stabilise carbon dioxide

emissions at 1990 levels by the end of the century in response to concerns about the issue of global warming.

One of the first pieces of legislation introduced to protect the water environment in the UK was the 1973 Water Act which saw the creation of 10 separate water authorities to deal with issues related to water supply and waste water treatment. This 1973 Act was updated in 1989 with the formation of the independent regulatory body the National Rivers Authority (NRA) to monitor and control the pollution of Britain's waters. Five more Acts dedicated to the protection of water resources were introduced in 1991, namely:

1. the Water Industry Act;
2. the Water Resources Act;
3. the Statutory Water Companies Act;
4. the Land Drainage Act; and
5. the Water Consolidation Act.

These five acts were designed to simplify the tasks of the NRA by covering all aspects of the protection and the use of water in the UK.

Solid waste was originally controlled via the Control of Pollution Act (COPA) of 1974 which introduced the concept of waste disposal plans and licences for household, commercial and industrial wastes. The Environmental Protection Act (EPA) of 1990 introduced the concept of waste management as opposed to the traditional methods of waste disposal. In this way the regulators sought to reduce the total amount of waste being produced rather than treat that waste.

One of the main driving forces behind the development of environmental impact indices in the UK was the introduction of Integrated Pollution Control (IPC) in Part 1 of the Environmental Protection Act (1990). IPC was introduced to "develop an approach to pollution control that considers releases to all media from industrial processes in the context of the effect on the environment as a whole" (HMIP, 1994a). To ensure that all releases from industrial processes result in the minimum environmental impact operators have to prove that they are utilising the Best Available Techniques Not Entailing Excessive Cost (BATNEEC). The introduction

of BATNEEC required the development of a range of tools for identifying which of the technologies available was the best for each given operation. Such tools must be capable of quantitatively assessing a given process operation to enable comparison of its environmental 'friendliness' with other alternatives.

The EPA (1990) represented the first formal approach to the protection of the environment as a whole. This legislation was soon followed by the formation of the regulatory body the Environment Agency in 1996 under the conditions of the Environment Act (1995). The Environment Agency was formed to provide "an integrated approach to environmental protection and enhancement, taking into consideration the impact of all activities and natural resources" (Environment Agency, 1996). It was created to combine the power and expertise of the National Rivers Authority, Her Majesty's Inspectorate of Pollution (HMIP), the Water Regulation Authorities and some units from the Department of the Environment.

Similar developments have occurred in the USA. In 1969 the US Congress passed the National Environmental Policy Act in order to develop a national approach for the preservation of the environment (Rau and Wooten, 1980). This showed that the environmental problems were as much of a concern in the industrialised USA as they were in Britain. Around 1970 the USA officially recognised the problem caused by the accumulation of wastes from chemical processes over the previous two centuries by conducting their first national study of the problem. Today the US Environmental Protection Agency (US EPA) performs a similar function to the Environment Agency in Britain.

One of the most significant global attempts to develop plans for the protection of the environment arose from a study carried out by the United Nations' Brundtland Commission (World Commission on Environment and Development, 1987). The Commission introduced the concept of sustainable development which was defined as that which "meets the needs of the present without compromising the ability of future generations to meet their own needs". Christ (1996) identified that the concept of sustainable development had implications in the areas of financial, social and environmental management. In the environmental sense he defined the concept as

development "not exceeding the limits of environmental impact and maintaining the natural basis of life".

In order to define development which is within the limits of environmental impact it is first necessary to quantify these limits. To do this a range of quantitative tools are required to assess effectively the types and extent of impacts that human development has on the environment. Several tools have been developed to include environmental concerns in the design of chemical processes. Methodologies have concentrated mainly on three major approaches:

1. waste minimisation design techniques;
2. environmental quality assessment; and
3. environmental impact assessment.

Waste minimisation techniques are based on designing and operating inherently clean processes. The techniques are used to examine where it is possible to reduce the amount of waste which is produced during the normal operation of processes and during accidents. The environmental quality and impact assessment methods are used to analyse the effects of given processes on the environment.

Waste minimisation techniques

Three design techniques which are based around the principles of waste minimisation are:

- Mass Exchange Networks (MEN) (El-Halwagi and Manousiouthakis, 1989);
- Graphical Mass Balances (GMB) (Flower, Bikos and Johnson, 1993); and
- ENVironmental OPtimisation (ENVOP) (Potter and Isalski, 1993).

Mass exchange networks are similar to heat exchange networks and involve the "systematic generation of a cost-effective network of mass exchangers with the purpose of preferentially transferring certain species from a set of rich streams to a set of lean streams" (El-Halwagi and Manousiouthakis, 1989). Thus in order to minimise the waste which is being produced by a process it is transferred between different streams to allow for the optimal use of mass transfer agents or solvents.

The graphical mass balance is a simple method for visually displaying the material flows for a given process. It allows for the easy manipulation of process parameters such as stream splits and reaction conversions in the assessment of different process options. The impact of these changes on the quantities of wastes being produced can then be analysed to find an optimal operating configuration.

The ENVOP technique was developed as part of a joint project between BP and Costain. It is a six step process for analysing flowsheets to reduce the possible environmental impacts in the same way that the HAZard and OPerability (HAZOP) studies are used to produce safety assessments of processes (Lawley, 1974). The six steps are summarised in Table 1.1.

Table 1.1 The six steps of the ENVOP technique

	Step	Description
1	Definition	Define the problem, the process and the environmental objectives.
2	Formal review	Divide the flowsheet into process blocks and analyse using keywords/deviations approach as for HAZOP. Identify appropriate actions.
3	Initial screening	Prioritise actions identified in 2.
4	Technical and economic analysis	Test actions on a model of the process and analyse financial and technical costs.
5	Review	Review the recommendations from steps 1 - 4.
6	Report	Report the findings of the analysis.

Environmental quality and impact assessment

Sections 1.2 and 1.3 describe briefly what an environmental index entails and why there is such a need for these tools in industry today. Chapter 2 then traces in greater detail the development of several of these impact assessment tools.

1.2 What is an environmental index?

An Environmental Impact Index is a tool which can be used to quantitatively assess the effect that a process has on the environment. Thom and Ott (1975) defined an air pollution index as "a scheme that transforms the weighted values of individual air pollution-related parameters into a single number or set of numbers". This definition can be extended to all environmental indices as shown conceptually in Figure 1.1.

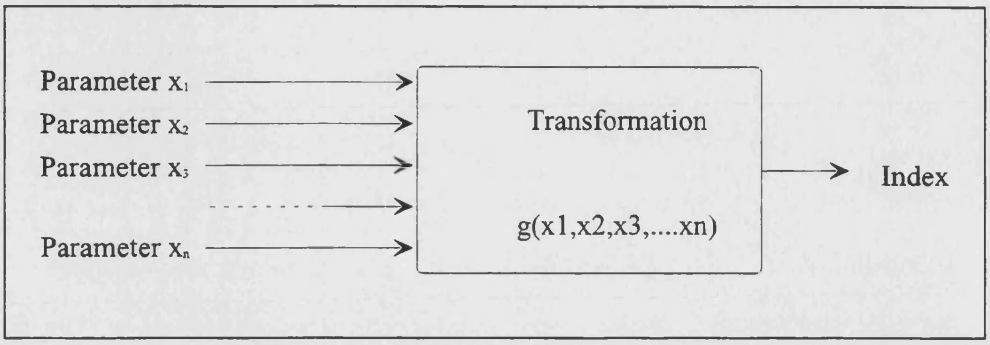

Figure 1.1 Basic principles of environmental indices (Thom and Ott, 1975)

The conceptualisation stages identified in the transformation process in Figure 1.1 provide the framework for the four main techniques that could be used to develop an index. These four techniques which are presented in the four right-hand boxes in Figure 1.2 involve the identification and measurement of key environmental parameters. The selection of these parameters is then followed by the transformation of the raw data into consistent measures of environmental impact which are then combined to yield an overall environmental quality index. At each stage it is necessary to refer back to the initial concepts to ensure that a balanced and reliable analysis is developed.

The transformation which takes place involves converting the concepts of both qualitative and quantitative parameters which are indicative of particular environmental effects into mathematical values which can be used to assign a numerical value or score to environmental impact. Therefore, the construction of a tool for the assessment of environmental impact must involve the development not only of the relevant concepts but also of the system for assigning the appropriate scores. Figure 1.2 illustrates the links between the major development steps for an environmental assessment tool as identified by Craik and Zube (1976).

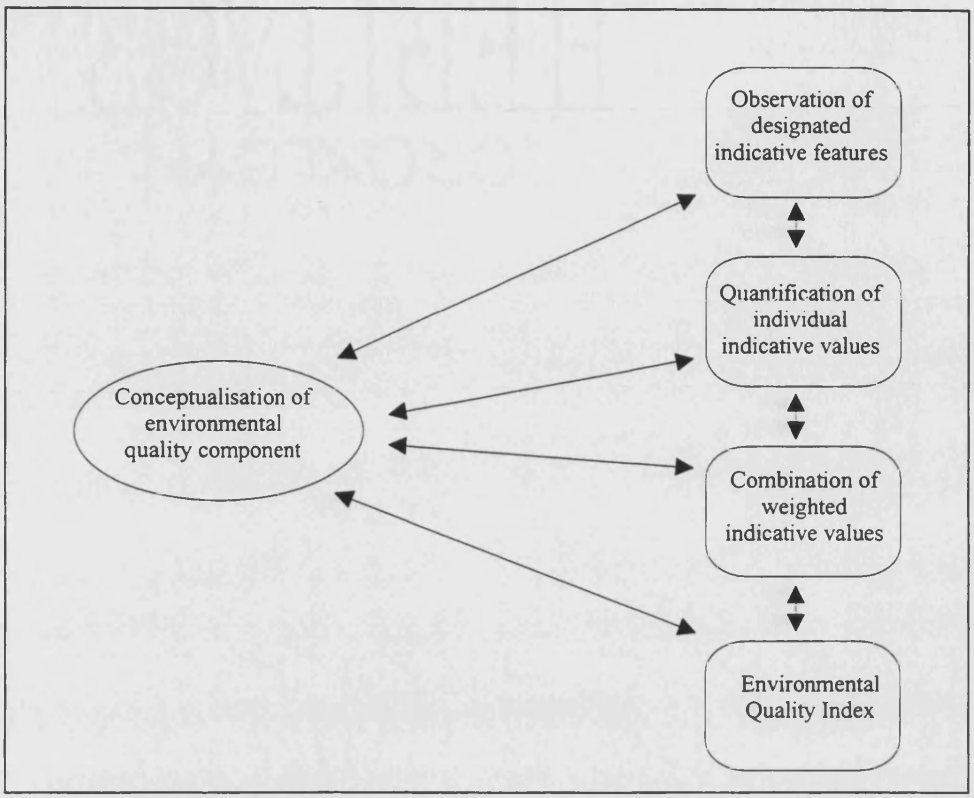

Figure 1.2 How the indices work

1.3 The need for indices

Many researchers have identified the need for quantitative tools for assessing the impact that chemical processes have on the environment and some of these refer specifically to the need for environmental indices.

Allen (1992) highlighted several "technical roadblocks" when reducing pollution from chemical processes. Along with the need to adopt commonly accepted waste minimisation practices such as good housekeeping and the use of current technology, Allen indicated the need for "the development of pollution prevention measurement tools, so that critical emissions and waste streams can be targeted for prevention". One of the tools he suggested for this purpose was indexing.

In a similar way, Brennan (1993) highlighted "four challenges for the design and evaluation of cleaner production processes".

These four challenges were:

- the need for improved environmental assessment methodology;

- the need to define and extend system boundaries;
- the need for inherently environment-friendly processes; and
- the need to integrate economic, technical, safety and environmental objectives.

For the first of the challenges Brennan identified a "pressing need for a quantitative index which can distinguish between the environmental merits of alternative processes in new process development and in early phases of project development". He also stressed that a multimedia index was required as chemicals "impact differently on the environment depending on whether they are released to air, waterways or land".

Cohen and Allen (1992) proposed a research programme concentrating on waste minimisation and treatment technologies, including the need for the "identification of key pollutants and waste streams" and the "development of design methodologies". In targeting the waste streams, four major steps were identified. These four steps were:

- establish emission rates;
- estimate the partitioning and fate of emissions in the ambient environment;
- calculate the human exposure to the emission; and
- estimate a measure of the risk associated with the exposure.

Having identified the need for a quantitative environmental impact assessment tool it is necessary to define some basic objectives of the assessment which not only deal with the content of the index but also the means of integrating it as an effective and useful tool within the design process.

1.4 Aims and Objectives

The aim of this thesis is to develop EniVal, a tool similar to these indices which will be used to assess and minimise the environmental impact of continuous chemical processes. EniVal (Environmental Impact Valuation) will be a useful tool for the selection of the best environmental option either from a number of new process options or from a selection of retrofits. This will allow environmental impact to

become a significant quantitative component in the design process which has hitherto been dominated by cost issues.

The development of EniVal will accomplish the following objectives. It will:

1. assess the environmental impact of chemical processes on the whole of the environment, including all discharges to atmosphere, water and land;
2. not rely on environmental concentrations which are often unreliable, unavailable and costly to obtain; and
3. be computer-based while maintaining simplicity to allow all users to obtain the maximum benefit from it.

Section 1.5 presents a brief summary of this thesis highlighting the main themes of each chapter and how they relate to each other.

1.5 Overview of the structure of this thesis

The emergence of environmental issues as a dominant driving force in process design has been introduced in this chapter. A brief history of these environmental concerns provides the background for the development of a range of tools which are used by designers to develop environmentally sound processes. Chapter 2 investigates these tools in greater detail and follows their development from simple scoring methods to completely integrated environmental design methodologies. It analyses the different approaches which have been taken in order to assess and quantify environmental impact and provides reviews of the typical techniques which utilise these approaches.

The initial stages of the development of EniVal are outlined in Chapter 3. Boundaries for the analysis are defined both in terms of the spatial distribution of pollutants and in terms of the timescales of the analyses of the impacts caused by the discharge of these pollutants. All of the information contained within EniVal is presented on a tree structure. Chapter 3 illustrates in detail the upper levels of this tree which split the overall index into long-term and short-term assessments. These branches are then split further into effect branches which contain the data related to the impacts of the discharges on each sub-system of the environment. In order to

provide an integrated approach to assessing the impact of the discharges on the whole environment EniVal utilises a series of models for predicting the long-term fate of pollutants in the atmosphere, water and soil. The development and scope of these models is presented in this chapter together with a commentary on the difficulties encountered in developing them.

The lower levels of the tree structure which contain all of the parameters used to quantify the environmental impact of a given chemical are described in Chapter 4. The reasons for the selection of these parameters are presented along with the scoring systems which have been developed to provide quantitative measures of the environmental effects being described.

Chapter 5 defines the mathematical techniques needed to combine the raw data from all of the parameters discussed in Chapter 4 with the data from the fate and distribution models to provide an impact score for each chemical. A sample calculation of the impact score for a sample chemical is provided to show how the parameter scores are combined at each successive level of the tree structure.

In order to complete the design of the index the tree structure has been tested using operating data from a selection of twelve chemical processes. These processes range from simple boilers to complex organic chemical production and represent a variety of different types of discharges. A short description of the 12 processes and justification for their inclusion are provided in Chapter 6 along with simple process schematic diagrams.

In Chapter 7 these chemical processes are analysed in order to determine the most effective means of combining the impact scores with pollutant discharge data at the top level of the index. Alternative ways of combining the impact and mass data are examined with regard to the range and spread of EniVal values, the effects of errors in the raw data on final values and the sensitivity of EniVal to changes in emissions.

Chapter 8 provides a brief summary of how the concept of the EniVal tree structure was transformed from a series of mathematical operations into a computer-based tool

for use by process design engineers. It illustrates how a visual programming package is used to create a graphical user interface which allows for the complex analyses to be represented simply. Two simple case studies are provided to show how EniVal can be used as a process design tool. Two of the processes from Chapter 5 are used to illustrate the effect that various process alterations would have on the environmental impact of these processes.

An overall summary of the project and a discussion of how EniVal can be further enhanced through future work is included in Chapter 9.

Chapter 2

History of indices

The majority of early environmental quality indices were developed in the USA in the 1970s. They were developed following concerns over the decreasing quality of the environment due to heavy industrialisation. The initial purposes of these indices and tools were to measure the quality of the environment itself and to monitor any changes which were taking place.

Gradually through the 1970s and 1980s these tools began to be increasingly used to examine individual locations which may have been affected by industry. The tools were modified progressively for use in assessing particular processes and particular chemicals. Hence this development resulted in the generation of tools designed specifically to measure environmental impact rather than environmental quality. The first tool which was used for this analysis of environmental impact was the chemical scoring system which simply provided a set of scores for the hazards associated with each chemical. These tools were then modified to produce environmental impact indices which assess the impact of a given chemical process on the environment.

In this Chapter section 2.1 examines three typical environmental quality indices. Section 2.2 outlines some of the work that has been carried out in order to move towards a more chemical orientated assessment of impact. Section 2.3 examines some of the more recent tools which have been extended further than the chemical scoring systems into overall process assessment. Many design techniques are beginning to incorporate principles of environmental assessment. Some of these techniques and the assessment tools that they use are presented in section 2.4. The final section in this Chapter provides a brief summary of all the assessment methods and an outline of what is required of an optimal environmental analysis tool.

2.1 Environmental quality indices

The focus for environmental quality indices lies firmly in quantifying the state of the environment at a given location. Generally this involves measuring parameters related to air quality and water quality and incorporating these within separate

indices for each medium. This section illustrates one air quality index and one water quality index in detail and examines briefly an overall environmental quality index. A more comprehensive summary of existing environmental quality indices (including those illustrated in this section) is provided in Appendix A.

Table 2.1 shows a typical index used to assess water quality. As can be seen nitrates, biochemical oxygen demand (BOD), dissolved oxygen concentration (DO), phosphates (PO_4), temperature deviation from equilibrium, faecal coliform count, total solids and turbidity are the main parameters which are included in the analysis of water quality. These parameters are often used to assess not only the quality of water bodies but also the quality of any aqueous discharges from drains and sewers.

Table 2.1 Typical water quality index

Name	Unweighted Arithmetic Water Quality Index (WQIAU)
Variables (q)	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3^-, PO_4^-, temperature deviation from equilibrium, turbidity, total solids, dissolved oxygen (% saturation)
Equation	$WQIAU = \left(\frac{1}{9}\right)\sum_{i=1}^{9} q_i$
Description	The raw data for the parameters above are manipulated using a series of quality transformations to provide the quality values q_i required for the formula. The quality transformations were obtained from expert opinion. 70 persons with expertise in water quality management were asked to draw plots of quality against parameter value and the average curves were used for the transformations.
Reference	(Brown, McClelland, Deininger and Tozer, 1970)

A summary of a typical air quality index is shown in Table 2.2. Air quality indices are generally based on the concentrations of pollutants in the environment and a number of pollutants are consistently recognised as being critical to environmental quality. For air these pollutants include nitrogen oxides (NO_x), sulphur oxides (SO_x), carbon monoxide (CO), oxidants (OX) and total suspended particulates, (TSP).

Table 2.2 Typical air quality index

Name	Mitre Air Quality Index (MAQI)
Variables	CO, SO_2, TSP, NO_2, OX
Equation	$MAQI = \sqrt{\sum_i I_i^2}$ Ii = indicator for each pollutant I
Range	0-3+
Categories	<1 no std exceeded $1 \leq MAQI \leq 3$ standards met or exceeded > 3 one or more standard exceeded
Description	Index may be calculated for any combination of i = 1 to 5 pollutants; indicator I_i is based on secondary National Ambient Air Quality Standards (NAAQS): $I_i = \sqrt{\left[\left(\frac{c_{ia}}{S_{ia}}\right)^2 + \sigma_i \sum_i \left(\frac{c_{ih}}{S_{ih}}\right)^2\right]}$ where c_{ia} = mean conc. of pollutant i, during longest measurement period a, as specified by standard S_{ia} c_{ih} = mean conc. Of pollutant i, during hourly measurement period h, as specified by standard S_{ih} $\sigma_j = 1$ if $(c_{ih})_j > S_{ih}$ $\sigma_j = 0$ if $(c_{ih})_j < S_{ih}$
Reference	(Thom and Ott, 1975)

Hope, Peake and Parker (1992) produced an index which uses public opinion to assess the overall quality of the environment. They tried to consider many factors over the whole environment including an element of town planning. There are nine different parameters in the index shown in Table 2.3 and each is assigned a weighting.

Table 2.3 Parameters for environmental quality index

Parameters	Units
NOx emissions	'000 tonnes NO2 equivalent
SO_2 urban concentrations	$\mu g/m^3$
low-level O_3 concentrations	average monthly 99th percentile
CO_2 emissions	million tonnes of carbon
oil spills requiring clean-up	number
fractional length of river of poor or bad quality	percentage
resident population	millions
fertiliser deliveries to agricultural use	'000 tonnes
new dwellings started	'000

The weightings were developed through the use of results obtained from a series of public opinion surveys carried out across the world. An analysis was made of the

sensitivity of the weightings to different geographical locations to show that while different parameters have greater significance for different nationalities, the general trends are closely matched.

The quality indices described in this section are only useful for examining particular locations in the environment to determine how they have been affected by different influences. They have limited use for examining specific chemical operations. The chemical scoring systems discussed in the next section assess individual chemicals so that all of the discharges from a given process can be considered together.

2.2 Scoring systems

A significant proportion of the work which has been carried out on chemical scoring systems has been done in the USA. The research was mainly conducted as part of the testing processes which are carried out on all new chemicals.

Brown, Holt and McCaleb (1976) prepared a report entitled "Systems for Rapid Ranking of Environmental Pollutants" for the Stanford Research Institute. This report summarised a project that involved the development of a scoring system by a team of scientists, mathematicians and engineers. They initially investigated four possible systems:

- an expert-based system;
- a screening-based system;
- an index-based system; and
- a model-based system.

Each of these techniques concentrates on analysing three key areas of chemical behaviour, namely release and distribution, transport and transformation and effects. The expert-based system which was finally selected utilises a number of parameters to illustrate the hazards associated with each of these three key areas. These parameters, including threshold limit values, the lethal dose (LD_{50}), partition coefficients and vapour pressure are then scored and combined.

A similar study carried out by Nelson, van Duuren and Goldschmidt (1975) concentrated on three major areas of concern for each chemical. These were related to the nature of the release of the chemical, its effects on the environment and its effects on human health. Each of these issues was dealt with separately.

As part of a US EPA workshop on Environmental Scoring of Chemicals, Ross and Welch (1979) developed a system which is based on both environmental concentrations and total pollutant discharges. This system develops scores based on rankings for the chemicals. The purpose of the scoring (as defined by the workshop) was "to identify most of the chemicals that have a high probability of requiring review for regulation or testing ". The first stage of testing utilises a set of scoring systems based on a determined range of values for each parameter. This preliminary analysis does not require the use of environmental concentrations. However it was identified that for more rigorous testing, environmental concentrations should be used in the calculation of the effect scores. A total of 10 different chemicals were tested using the scoring system and significant variations were observed due to the subjective nature of the system. The chemicals used are shown in Table 2.4.

Table 2.4 Chemicals used to test US EPA scoring system

Chemical name	Formula
Ammonia	NH_3
Chlordane	$C_{10}H_6Cl_8$
Tetraethyl lead	$(C_2H_5)_4Pb$
Leptophos	$C_{13}H_{10}BrCl_2O_2PS$
Diethyl hexylphthalate	$C_6H_4(CO_2C_8H_{17})_2$
Nitrilotriacetic acid	$N(CH_2CO_2H)_3$
Hexachlorocyclopentadiene	C_5CL_6
Linear alkyl sulfonate	$C_6H_5SO_3$-R
2,4-Xylenol	$C_{31}H_{32}N_2O_{13}S$
Quinaldine	$C_6H_4NC(CH_3)CHCH$

Recent efforts have focused on the direct impact that a specific process has on the receiving environment. These newer methods not only consider the nature of the discharges from the process but combine this information with operational data related to a given process. Examples of these tools are presented in the following section.

2.3 Process environmental indices

In recent years attempts have been made to quantify the environmental impact of specific chemical processes. Methods have centred mainly around the concept of Environmental Impact Assessment (EIA), either through the preparation of Environmental Impact Statements (EIS) or other assessment tools. However there have also been a number of indices developed by both government bodies and by industrial companies which aim to assess the impact of an individual process or industrial site. These include the Best Practicable Environmental Option (BPEO) selection process which was developed by Her Majesty's Inspectorate of Pollution (1994b) and the Environmental Load Factor (Caughlin, 1993).

The four main approaches which have been adopted in the development of tools for impact assessment are:

- the load factor approach;
- the environmental performance approach;
- the environmental concentration factor approach, and;
- the mass and effect approach.

The following four sections highlight some of the main methods which have been adopted in these approaches. Following the descriptions of each method a summary of the major problems associated with each approach is used to illustrate their main shortcomings.

2.3.1 The environmental load factor approach

The load factor approach considers the quantity of waste produced by a given process. It has been used to compare the relative levels of waste production arising in different industries (Sheldon, 1994).

The Environmental Load Factor (ELF) as defined by Caughlin (1993) is calculated by dividing the total mass of wastes produced by a process over a given time by the amount of product produced over the same time period. Such a load factor does not consider any of the properties of the individual wastes, only their quantities.

Two enhancements of the load factor technique have been suggested by Cunningham (1994) and Sheldon (1992). Cunningham combined the concept of the load factor with a difficulty factor which is a measure of the difficulty associated with treating or dealing with the polluting stream. Sheldon uses a slightly different approach and combines an atom utilisation (AU) concept with an unfriendliness quotient. The AU is defined as the molecular weight of the product divided by the sum of the molecular weights of all the substances produced and is used as a measure of the selectivity of the chemical reactions in the process. This AU is then multiplied by the arbitrarily assigned unfriendliness quotient which provides an indication of the undesirability of the by-products. Sheldon identified that "obviously such figures are highly debatable and will vary from one company or even production site to another, depending partly on the ability to handle and recycle the material in question".

The ELF approach can only be used to perform the most basic preliminary analysis of chemical processes. Its major shortfall is that it does not provide any indication of the nature of the waste which is being discharged, or of the likely effect that the waste will have on the receiving environment. It merely provides an indication of the relative amount of waste being produced within the process. While this information can be useful to the designer in waste minimisation studies the method is inadequate to allow for a comprehensive analysis of environmental performance. The methods of Sheldon (1992) and Cunningham (1994) while extending the concept to include measures of 'unfriendliness' do not provide a scientific basis for determining the effects of the discharges.

2.3.2 The environmental performance approach

Another approach that has been used to assess environmental impact is to base the index on the effectiveness of the disposal techniques required for specific wastes generated by processes. Shanks & McEwan (1993), a waste disposal company developed the following index.

$$\frac{100}{QH}\times\left[QH-\left(Qh_{BAD(air)}+Qh_{BADwater)}+Qh_{BAD(land)}\right)-\left(\frac{Qh_{D(air)}}{t_{1(air)}}+\frac{Qh_{D(water)}}{t_{2(water)}}+\frac{Qh_{D(land)}}{t_{3(land)}}\right)\right] \quad (2.1)$$

where:

QH is the quantity of the hazardous constituents with between 1 and 51 carbon atoms per molecule (C1-C51) which are contained within the waste product;

Qh_D is the quantity of hazard constituents (C1-C51) discharged over time to air water and land during the use of the waste disposal technique considered. This excludes discharges that are bio-accumulative or ozone-depleting which are accounted for under Qh_{BAD};

Qh_{BAD} is the quantity of hazardous constituents which are bio-accumulative and are discharged to air water and land during the use of the waste disposal technique under consideration; and

t_1, t_2, t_3 are the times over which the discharges to the unmanaged environmental media of air, water or land take place. For joint disposal to land, the time period begins after the waste has left any container and is in contact with the putrescible medium. Wastes which continue discharges after more than 2 years are considered unsuitable for land disposal.

This formula measures both the quantity of hazardous constituents as an input to the disposal technique, together with the quantity of hazardous constituents discharged. The relative weightings for those discharges which are either bio-accumulative or damaging to upper atmosphere ozone are increased by not dividing them by the period of time over which the discharge takes place.

Rhône-Poulenc Chemicals Ltd (1992) and Searle (Coates, 1994) have developed indices to assess their overall environmental performance. Their methods are described briefly in Table 2.5. A similar technique developed by Arthur D Little (ADL) uses an Environmental Performance Index (EPI). This index utilises four measures of 'cleanness' and assigns them various weightings. Environmental releases (total amounts) are given a weighting of 50%, regulatory compliance 25%, and resource consumption and remediation efforts 12.5% each.

Table 2.5 Process performance indicators

Company	Index	Parameters	Combination
Searle	Wastes to off-site disposal	Total wastes	Annual tonnage multiplied by an environmental acceptability factor
	Discharges to sewer	Discharge limits	Percentage that each parameter is within control limit set by regulatory authority
	Discharges to atmosphere	Total discharges	Scored according to severity and averaged annually
	Environmental incidents	All incidents	Scored according to severity - spillage to hazardous spill to watercourse
Rhône-Poulenc	Total Environmental Index	Chemical Oxygen Demand Total suspended Solids Nitrogen as Ammonium Mercury Landfilled wastes Incinerated wastes Halogenated wastes Other wastes	Each of these parameters is assigned a weighting. The sum of the parameters multiplied by their weightings gives the total environmental index.
	Special Waste Index	Special waste	Total discharge of special wastes relative to previous year
	Red list substance Index	Mercury	Total discharge of mercury relative to previous year

In general, tools based on environmental performance approaches are very simplistic and are used to communicate to a non-scientific audience. They are often utilised in a management environment for reporting on historical performance trends rather than for the design and improvement in the operation of chemical processes. If they are recognised as such then these tools do have a place in the environmental assessment field. However for a number of reasons which are outlined below the results from these techniques should always be treated with some scepticism.

The ADL assessment technique provides scores which could be used by a company to "measure its own performance relative to a chosen benchmark year and from year to year". ADL did identify that "there are better tools for actual performance

improvement purposes and for communication to a technically sophisticated audience" (ADL, 1995).

The formula used by Shanks & McEwan to assess environmental impact excludes carbon dioxide as a pollutant and therefore leaves some doubt as to the credibility of their indices. This exclusion is significant because the company concentrates mainly on the incineration of waste and uses the index to illustrate that incineration is often the most preferable environmental option. The Rhône-Poulenc indices have been criticised for the way in which they could be manipulated in order to illustrate improved environmental performance. Greenpeace went as far as to describe the index as "bizarre" and "another case of industry being afraid to disclose the real information" (*The Chemical Engineer*, 1993). Rhône-Poulenc's chairman and managing director, Keith Humphreys, described the index as being "very important to us as a management tool" and not an instrument to be used for public relations (*The Chemical Engineer*, 1993). The data obtained from the indices was presented in the IPC application (HMIP, 1992a) for the Rhône-Poulenc benzene, toluene and cyclohexane (BTC) plant from 1987 to 1991 along with sample calculations. Irrespective of the reasons for using these indices doubts remain as to their validity.

2.3.3 The environmental concentration factor approach

Many of the discharge licences and permits required for the operation of chemical processes are based on concentration data as it provides the most reliable method for assessing impacts on the receiving environment. Accordingly the environmental concentration factor approach is generally utilised by regulatory bodies such as the Environment Agency in the UK.

The BPEO selection process originally developed by HMIP (1994b) involves the calculation of six different parameters in order to describe fully the impact of an operation on the whole environment. These parameters are:

1. the Integrated Environmental Index (IEI);
2. the adverse short term effects;
3. the global warming potential;
4. the photochemical ozone creation potential;

5. the unit hazard score; and
6. other factors related to environmental quality.

The IEI compares the predicted environmental concentrations of all chemicals released with the relevant health standards based on effects on humans as shown in equation (2.2),

$$IEI_{(process)} = \sum_{m=1}^{i} \sum_{s=1}^{i} \frac{\text{Plant contribution}_{s,m}}{EQS_{s,m} \text{ or } EAL_{s,m}} \qquad (2.2)$$

where:

Plant contribution$_{s,m}$	is the maximum long term average environmental concentration of substance s released to medium m;
EQS	is the Environmental Quality Standard; and
EAL	is the Environmental Assessment Level (set by HMIP) utilised when no EQS exists.

The German Federal Environmental Agency proposed a technique similar to that proposed by HMIP whereby a predicted environmental concentration (PEC) is compared with a predicted no effect concentration (PNEC) (Ahlers, Diderich, Klaschka, Marschner, Schwarz-Schulz, 1994). The PEC is estimated using a series of models developed by Mackay (Mackay, 1979) which consider many of the actions and interactions of chemicals within the environment. These interactions include volatilisation from water, adsorption/desorption, biodegradation, hydrolysis, photodegradation in the hydrosphere and photodegradation in the atmosphere. These factors are considered over a range of timescales and also on both regional and local levels.

The PNEC is then determined by considering aquatic, terrestrial and atmospheric effects. The aquatic risk is assessed using lethal concentrations (LC_{50}), ecotoxicities (EC_{50}) and long-term toxicity data for Daphnia, fish and algae. The terrestrial effects are quantified using mammalian and bird LD_{50} data. Ahlers et al argue that due to the limited range of toxicity data available the atmospheric risk should be assessed using expert judgement on a series of typical effects. These effects include air quality degradation, tropospheric ozone building, acidification, depletion of the

ozone layer and the contribution to global warming. Various techniques were also identified for the extrapolation of data across media for use when only limited effect data are available. Similarly assessment factors are assigned to the parameters to provide a measure of the confidence in the data.

Indices which utilise environmental concentrations including the Integrated Environmental Index of HMIP (1994b) and the environmental risk assessment method of Ahlers et al (1994) allow for a more thorough investigation of impact but also have their faults. The indices are based on concentrations of the pollutants in the receiving environment. For new processes which are still at the design stage, and also for many existing processes the emission data which are required for this type of analysis are not available. This means that the majority of the data must be obtained using dispersion and multi-media models.

Although recent advances have meant that highly accurate modelling of the movement of chemicals in the environment is now possible it should be recognised that such work is costly and time consuming. As a result, the uncertainties in most of the data which arise from these models makes them unsuitable for use in this impact analysis. This concern was highlighted at an EPA workshop on scoring chemicals, where "further discussion, however, indicated that the environmental concentration of a chemical is usually not available and that the estimation of an environmental concentration is not readily accomplished" (Ross and Welch, 1979).

The HMIP consultation document (HMIP, 1994b) defined six parameters for analysing the environmental impact of chemical processes as described previously. Each of these parameters can be assessed individually for a given process. However, the consultation document provides little indication as to how these six parameters should be grouped and analysed in order to determine the best practicable option.

2.3.4 The mass and effect approach

Mass and effect approaches use information on both the amounts of chemicals which are discharged and the effects that those discharges have on the receiving environment. The methods often combine the techniques used in both the load factor

approach and in chemical scoring systems. Examples of methods which utilise this mixture of approaches are outlined below.

Baumann and Rydberg (1994) examined three alternative approaches to assessing environmental impact using life cycle techniques. These were the ECOlogical scarcity (ECO) method, the Environmental Theme (ET) method and the Environmental Priority Strategies in product design (EPS) method.

The ECO method compares the actual load of each chemical that a process contributes to the surrounding environment with predefined critical loads. These critical loads are based either on the capability of the ecology to accept and deal with the chemical or on limits which are deemed to be politically acceptable. Depending on the choice of critical load, the term 'load' can be defined as the amount of chemical or some other measure of the burden it places on the environment. This method is similar to that adopted by HMIP in the Integrated Environmental Index although the former uses a more thorough set of critical loads rather than the hierarchy of quality and health standards used in the HMIP method and it is based on mass loads rather than environmental concentrations.

The ET method incorporates a similar load approach but is split into environmental themes. Baumann (1994) presented several case studies utilising this method including on which incorporated the following themes:

- global warming;
- ozone depletion;
- acidification;
- eutrophication;
- disruption;
- disposal of waste; and
- depletion of natural resources.

In this study "ad hoc" weighting factors were then applied to each of these themes. Another of the case studies used political limits to derive the critical loads.

The final of the three methods examined by Baumann and Rydberg (1994), the EPS method, consists of two separate indices. The first of these is the emission index. This utilises six factors which are multiplied together to provide an overall emission index. One factor represents the image of society's evaluation of the given environmental problem, three more factors assess the extent of the problem and another is a measure of the contribution of a particular chemical to the given problem. The final factor represents the average cost of reducing the discharge of the chemical using end-of-pipe technologies. This index is then combined with a resource index which is a quantitative comparison of the resource irreplacability to its availability.

Smith (1996) developed a tool for assessing environmental risk for use within environmental management systems. This tool combines measures of the quantity of a given chemical, the occurrences which may result in its release and the hazards that may arise as a result of that release. These three measures (the quantity rating, the consequence factors and the hazard factors) are multiplied together and summed over all products and raw materials to give a measure of the total risk.

In the Netherlands, Novem (Netherlands Agency for Energy and the Environment) and RIVM (National Institute of Public Health and Environmental Protection) have adopted lifecycle techniques to develop the Eco-indicator 95 (Goedkoop, 1995). This tool was developed to integrate environmental aspects into the design process and considers the impacts and effects of all emissions and raw materials to enable the development of better and cleaner products. As shown in Figure 2.1, the Eco-indicator methodology consists of 5 steps. The first of these identifies all of the impacts which arise from a given operation and the second sorts these impacts into the relevant effect categories. The next step estimates the damage which results from these effects and the fourth assigns a value to the damage. The combination of all these factors provides the overall eco-indicator. The seriousness of an effect is measured using the distance-to-target method i.e. the difference between the current value and the target value provides a measure of the extent of the problem. The target values can be determined either scientifically or politically. As well as these distance-to-target weightings an additional subjective weighting factor is used

because "other factors in addition to the distance-to-target can also determine the seriousness of an effect". This means that the weightings have an unlimited degree of subjectivity.

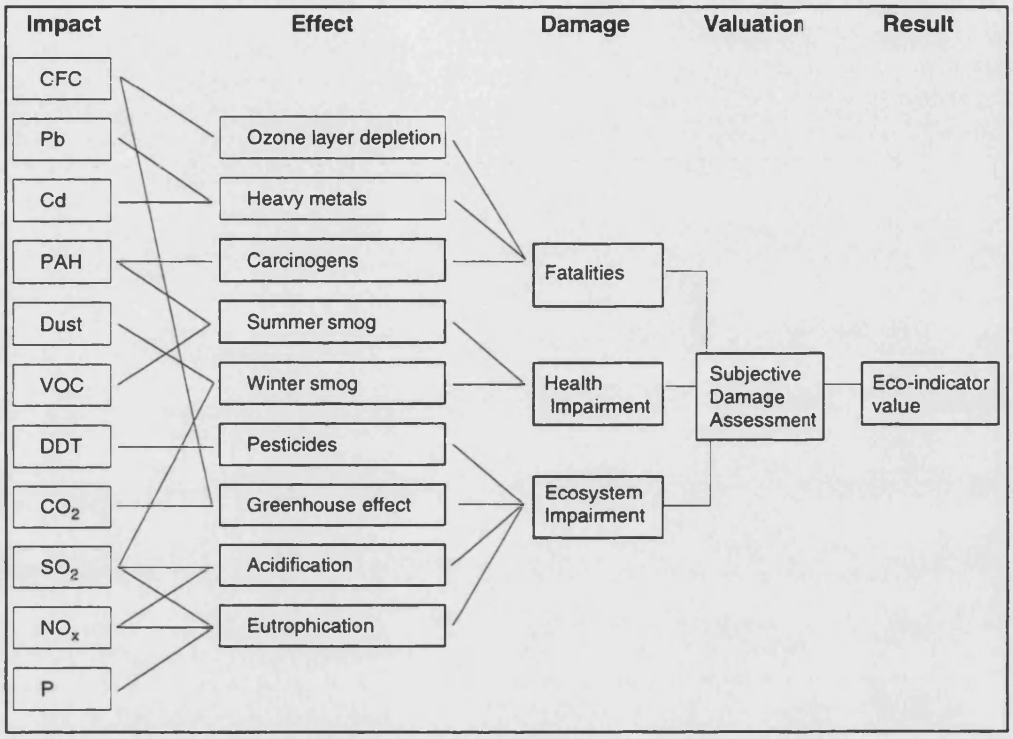

Figure 2.1 The Eco-indicator 95 (Goedkoop, 1995)

A methodology proposed by Pistikopoulos Stefanis and Livingstone (1995) incorporates six parameters as shown in Table 2.6 for assessing the environmental impact of a given chemical.

Table 2.6 Parameters for impact analysis

	Description		Formula
CTAM	Critical Air Mass	kg pollutant/h kg pollutant/kg air	emission mass standard limit value
CTWM	Critical Water Mass	kg pollutant/h kg pollutant/kg water	emission mass standard limit value
SMD	Solid Mass Disposal	kg solids/h	emission mass
GWI	Global Warming Index	kg CO_2/h	emission mass×GWP
POI	Photochemical Oxidation Impact	kg ethylene/h	-
SODI	Stratospheric Ozone Depletion Impact	kg CFC11/h	-

These parameters are incorporated with cost and other process data in a linear programming process optimisation tool.

Most of the techniques and tools described in this section recognise the need for an approach which considers both the amount of chemicals which are discharged and the likely effects that they will have on the environment. Each method uses different concepts to assess the effects. The three lifecycle methods examined by Baumann (1994) utilise assessments ranging from political and ecological critical limits to contribution factors developed through expert opinion. Smith (1996) utilises consequence and hazard factors which are scores reflecting the potential for and effect of various releases of chemicals. A factor is also included to take into account the quantity of each chemical.

However in all of these techniques there is no consistent approach adopted for assessing impact and little thought has been given to the combination of the discharge data with the effect information. The use of critical loads is a very subjective method for assessing environmental impact. It relies heavily on site specific information related to both the surrounding physical and political environments. This is of limited use when the overall environmental 'friendliness' of two or more particular designs is being compared. The method is very susceptible to manipulation by the user to achieve the desired responses. Similarly the use of consequence factors such as in the Environmental Rating method of Smith and the EPS method may also provide inconsistent results between different users.

2.4 Other work

As well as tools which have been developed specifically for environmental impact assessment there is a range of tools which have been developed for more general designs of chemical processes. Until recently the traditional priorities with these tools have been cost, safety and physical constraints. Increasingly however these tools are incorporating mechanisms for determining environmental impact. Many of the techniques described in the previous section can be utilised within these applications.

Linninger, Ali and Stephanopoulos (1996) have developed a knowledge-based system for designing batch pharmaceutical processes. Within the assessment of the process there is a module called the material assessor in which the impact of each

chemical is assessed using data and information obtained from the Syracuse Research Corporation in New York. This information includes data on the carcinogenicity, toxicity and other detrimental effects of each chemical. The system identifies problem chemicals which may need to be treated or replaced within the process.

Recently Heikkilä, Hurme and Järveläinen (1996) proposed a computer based tool for use in analysing safety considerations in process synthesis. Safety has always been a significant factor in process design and increasingly it is being combined with environmental issues in an overall assessment of safety and the environment. This tool incorporates six different databanks containing information on the hazardous properties of chemicals and the knowledge of safe and unsafe process concepts. From this the chemical inherent safety index is determined. The index "describes the effect of the choice of raw materials and other chemicals on the inherent safety of the process". It considers different physical and chemical properties of each chemical including the heats of the main and side reactions, flammability of the chemical (represented by flashpoint), explosiveness (represented by explosion limits), toxicity (represented by Threshold Limit Values), corrosiveness and incompatibility with other chemicals. These parameters are assigned scores and then summed over all of the chemicals in the process to determine the overall chemical safety index for the given process. This information is then combined with specific process information in order to determine the safest process.

Debeil and Myrén (1995) outlined a four step procedure for resolving safety and environmental conflicts. These four steps constitute a cycle by which process designs can be modified and improved as shown in Table 2.7.

Table 2.7 Safety and environmental assessment cycle

Step	Details
1	Identify safety issues
2	Measure emissions and consumption of natural resources
3	Use Best Available Technology (BAT) and inherent safety principles to improve process
4	Design the selected process, perform HAZard and OPerability study (HAZOP) and return to step 1.

The authors identified that "early in project planning there are options for efficient, clean and safe technology, 'integrated process technology' as opposed to end of pipe technology". The procedure incorporates a number of safety indices and an environmental index. The safety indices considered were the Dow Fire and Explosion index and the Dow Toxicity index. They proposed to use a tool such as EniVal for the assessment of environmental impact.

2.5 Summary

In order to overcome the practical limitations of existing indices, an integrated index is needed which is capable of assessing the impact of chemical processes across the whole environment in a consistent and logical manner. From the four categories of approaches outlined above such an integrated index must adopt the techniques associated with the mass and effect indices in order to provide the most comprehensive analysis of the overall impact. The challenge is to develop a tool which can consistently and reliably assess the impacts of discharges and most effectively combine this information with process discharge data.

Chapter 3

The development of EniVal

Several steps must be followed in the development of an environmental index as identified in the Chapter 2. The overall concepts behind the assessment techniques need to be identified and then qualified by selecting the boundaries for the analysis. Once this conceptual knowledge has been identified the structure can be developed further by quantifying the measures of impact. This chapter deals with the development of the underlying concepts behind the assessment of the environmental impact of a chemical process and the structure on which these concepts will be qualified. This chapter also examines the overall scope of the work and identifies the important boundaries for the environmental compartments. The analysis of the movement of chemicals within these compartments is then quantified through the development of long-term fate and distribution models for both organic and inorganic chemicals.

3.1 The scope of EniVal

Environmental impact assessment is a very complicated issue in which many different factors need to be considered. With so many techniques already existing such as the range offered by HMIP (1994b) it is important to identify the factors which are the most significant. It is also necessary to define the boundaries for the study both in terms of physical regions and in terms of the extent to which the effects of given chemicals on the environment will be considered. Environmental impacts incorporate many different issues including damage to the ecology, aesthetic impacts caused by unsightly discharges and detrimental effects on human health. In the following sections the boundaries for EniVal are defined and the major issues within these boundaries are identified.

3.1.1 Process boundaries

One of the main aims of EniVal is to consider the effects of pollution on the environment as a whole. Thus the boundary for the study has been extended to include not only all discharges crossing the process fence-line but also the fate of these discharges within the whole of the receiving environment. EniVal analyses the

consequences of the release of all chemicals from a given process. The boundary for the analysis has been selected to include all the continuous emissions from a given site and does not incoporate any measures of resource depletion or raw material factors. The contribution of planned and accidental effects such as spills or point releases has also not been included and need to be considered separately.

3.1.2 Timescale

In order to assess the overall impact that a given chemical will have on the environment it is necessary to study its effects over a range of timescales. Even for the comparatively simpler assessment of the toxicity of chemicals to humans there are many tests which are carried out for different periods ranging from minutes to years. In order to incorporate an assessment of the variation in the effects of chemicals over different time periods, EniVal considers both the short-term and the long-term effects as well as distributions of pollutants in the environment. Thus EniVal provides an overall assessment of both the localised short-term impact of a chemical process and the long-term consequences of releases. Short-term effects have been defined as those which occur within hours or days of exposure while long-term effects encompass impacts that may take up to several years or decades to fully appear.

3.2 Conceptualisation of EniVal

The underlying concept behind EniVal is a tree structure with each level of the tree representing ever more complex details in the analysis of the process. One of the main criticisms of the majority of previous work carried out on environmental impact indices is related to the limited usefulness of the results of the analyses (ENDS, 1995). In the past most indices analysed large amounts of data and then provided a single number. This number was accepted to be representative of the effect being quantified by the index. Such an approach has limited value however as it provides little or no information about the complex analysis of all of the data related to the operation of the process. While previous indices do provide a measure of the overall impact this is of limited use if the source of the data value cannot be traced back through the analysis. The contention is that the overall impact of a process cannot be fully quantified using a single value.

3.2.1 Tree structure

The tree structure allows all of the information incorporated within the analysis to be made available to the user. Thus, the path of the analysis can be traced back from the final value so that the areas of key concern can be identified as shown in Figure 3.1.

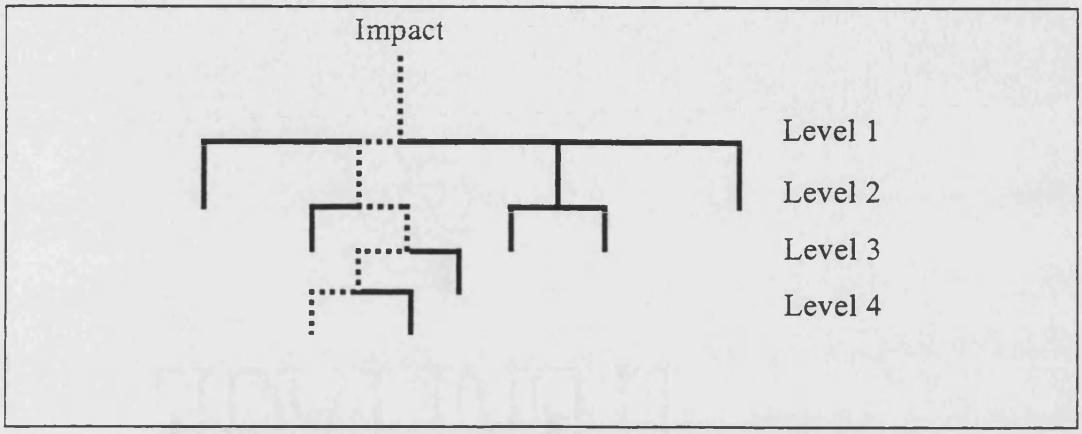

Figure 3.1 Tree structure of EniVal showing path tracing

A tree structured system provides not only the overall impact score at the apex of the tree, but also a range of data and information at each level down through the analysis. This approach allows the user to identify those areas of the process which are causing the most significant damage to the environment. Once these areas have been identified they can be targeted in the design process. Figure G.1 shown in Appendix G presents the overall tree structure for EniVal along with details of the combination techniques defined in Chapters 5 and 7.

The main aim of EniVal is to provide an overall measure of the impacts that the operation of a given chemical process will have on the environment. In order to do this it is necessary to analyse the impacts of all discharges from the process on the whole environment over both short and long time periods as discussed in section 3.1.2. As the assessment of these effects will generally require different techniques they cannot be combined until the final stages in the analysis. This aspect is shown in Figure 3.2 wherein the general outline of the top four levels of the tree structure for EniVal are shown. As can be seen EniVal has been split into a number of levels each dealing with increasingly detailed information about the process.

The two main components of impact (long-term impact and short-term impact) are considered at the second level of the investigation. Within each of these components the effects of each discharge are assessed over the whole environment. To do this the individual effects on each sub-system within the environment (atmosphere, water and soil) are analysed and then combined together using a series of both short-term and long-term fate models to give a measure of the total environmental impact. Individual effects are assessed by selecting key parameters which are indicative of the impacts and developing scoring systems to provide a quantitative measure of the overall effects rather than the individual results of exposure. All of these measures are analysed to provide an overall impact score for each chemical in each medium for both the short-term and the long-term. These impact data are then combined with discharge data for each release to give a scaled score for the overall environmental impact of the process as shown in levels 1 and 2 of EniVal in Figure 3.2.

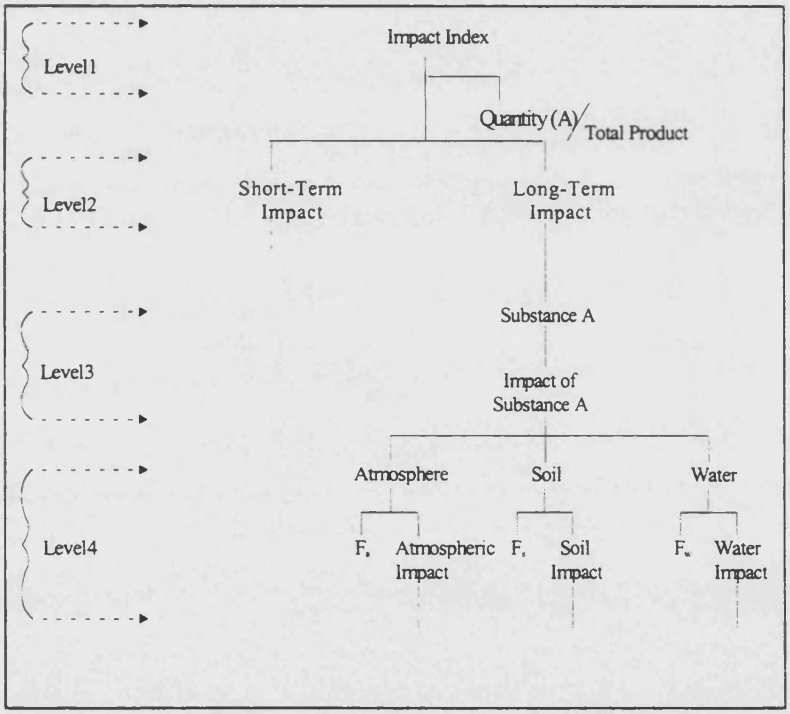

Figure 3.2 Top four levels of EniVal

Chemical discharges cause different impacts within each medium. However these impacts can often be classified within several effect categories and the selection of these categories as outlined in section 3.3 forms the basis for the whole impact analysis.

3.3 Qualifying environmental impact

The assessment of the impact that a given chemical will have on the environment is a particularly subjective process. Priorities for the analysis are always dependent on the needs and perspectives of the analyser. In order to encompass the whole of the environment within the scope of EniVal the overall impact is categorised by the types of effects that chemicals will have. These effects are grouped into one of three effect categories:

- Damage;
- Modification; and
- Persistence.

As shown in Figure 3.3 which illustrates the atmospheric impact branch of the tree these three effect categories provide the fifth level of information in the overall structure of EniVal.

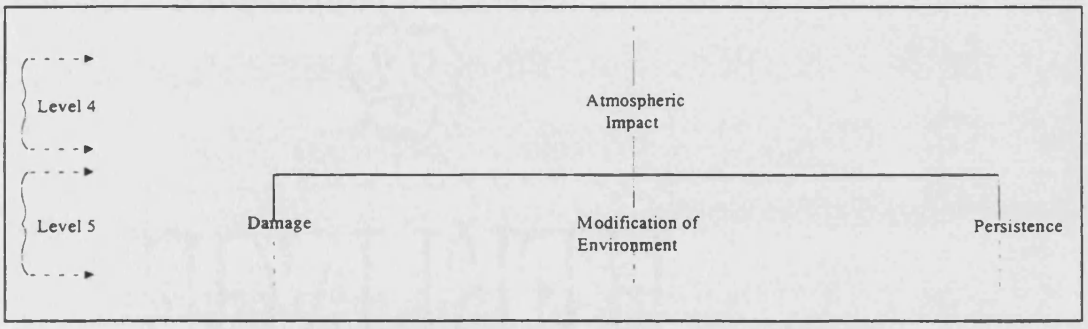

Figure 3.3 Atmospheric sub-system impact branch

3.3.1 Damage

The damage to the environment category investigates aspects of a chemical's direct impact on living creatures. For the purpose of this study, the term 'living creatures' is defined to include all animals, fish, birds and plants. However due to the limited data available for many species of animals and plants and given that many toxicological and effects studies are performed for determining human exposures the analysis is predominantly centred on the impacts on humans and their immediate environment. The main areas which need to be considered in this category are toxicity and hazardous characteristics.

3.3.2 Modification

The scope for the assessment of the impact of chemicals on the environment can be immense. Impact often covers many factors which are not considered solely under

the damage category outlined above. In order to allow for as many of these factors as possible, EniVal has been designed to include several parameters which assess the tendency of a chemical to modify the existing environment. Different parameters have been chosen for each medium in order to reflect many of the environmental issues which are currently of major concern to the public. The selection of these parameters depends on the scientific and political climates which exist at the time of the analysis and they should change with time to reflect the most current environmental concerns.

3.3.3 Persistence

The impact that a chemical has on its receiving environment is partially dependent on the duration of its presence in that environment as determined by its persistence. The persistence of chemicals in the three environmental media is estimated using parameters which are related to both the movement and the degradation of the individual chemical. The three categories considered are dispersion, degradation and bioconcentration. As discussed further in Section 3.4 the dissipation and degradation of a chemical in the environment is not included within the long-term fate models. Instead the measure of persistence is introduced within EniVal as a scaling factor for the overall effects.

3.4 Organic models

Several attempts including Hope, Parker and Peake's Pilot Environmental Index for the UK (1992) and the HMIP BPEO selection tools (1994b) have been made to consider the effect of chemical processes on the environment as a whole. One of the major flaws of these tools is that they do not consider the integration of the three media into one environment. Their approach is to take one index for each medium and then sum the results to derive an overall environmental index. This procedure clearly does not take into the account the many and varied interactions between the three media which are critical when assessing the final impact of pollutants on the environment. In order to overcome this limitation, EniVal has been designed to incorporate the ultimate or equilibrium fate of chemicals in the environment. The movement and final distribution of a chemical between atmosphere, water and soil is predicted using a series of models.

One of the major difficulties in the development of these models involved their complexity. If a model is too simple then it will not provide a useful indication of the fate of the chemicals. Alternatively, if the model is too complex then it will be difficult to obtain the required data, which leads to problems with usability and reliability. Thus, a balance had to be reached between making the models complex enough to provide useful information, yet simple enough to be manageable. The first step in the development of any model is to define its scope. For EniVal this was done by defining the system boundaries for the environment as a whole and then the sub-systems which exist within these boundaries.

3.4.1 Definition of the environment and scope of the models

The development of the models involved partitioning the environment into three sub-systems representing the Earth's atmosphere, water and soil. The models calculate an estimate of the overall long-term fraction of the mass of each chemical that will remain in each sub-system. Although the environment has been clearly partitioned into three sub-systems as outlined above, there are always some substances which strictly do not belong to one of these sub-systems. These substances include particulates in the atmosphere which can settle to the soil surface, and insoluble organic liquids which may be either more or less dense than water.

Figure 3.4 not only defines the boundaries of each sub-system but also illustrates the distribution of these separate phases which were not considered independently in the original definition. The figure also shows the directions of transport for the pollutants between the three sub-systems as indicated by the arrows connecting each sub-system with its adjacent one. As shown, the transport of the separate phases in each system is considered independently.

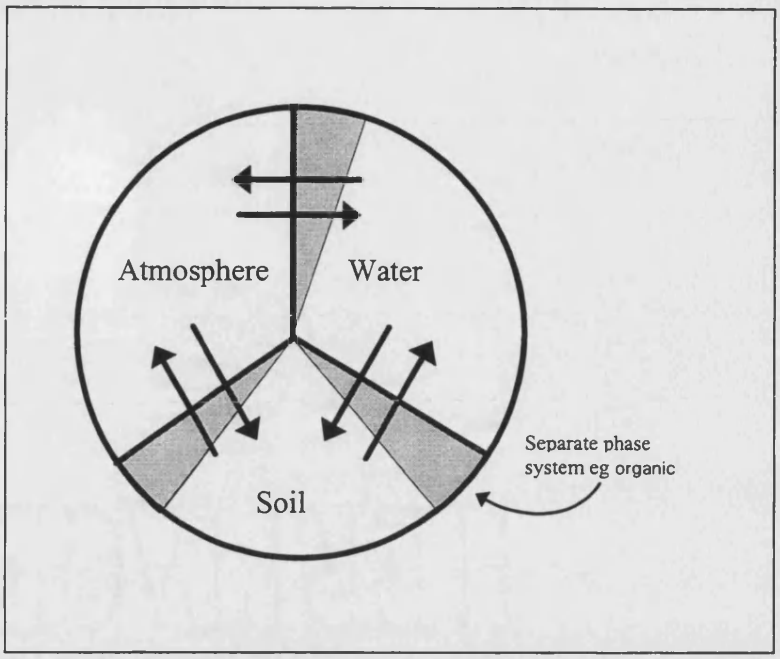

Figure 3.4 Definition of environmental systems and transport directions

The separate phases which are treated as part of the sub-systems within which they occur can be seen in Figure 3.5. A layer of organic material floating on the top of the water in the system as defined in Figure 3.5 was considered as part of the water sub-system. If the material sank in the water and was deposited on the bottom, then it would be assumed to be part of the soil sub-system. Similarly, if the material was originally in the air and it was then deposited on the soil, it would be considered as part of the soil environment.

The interactions between a separate third phase as illustrated in Figure 3.5 and the two adjacent sub-systems (water and atmosphere) will be different from those which would occur if the substance were completely miscible in either of the sub-systems. However, in order to maintain the simplicity in the model these differences were neglected. Accordingly, the organic layer was treated the same as if it were fully dissolved in the water as shown in Figure 3.5. The effects of the distribution of chemicals to the biotic phase were not considered within this system in order to maintain simplicity.

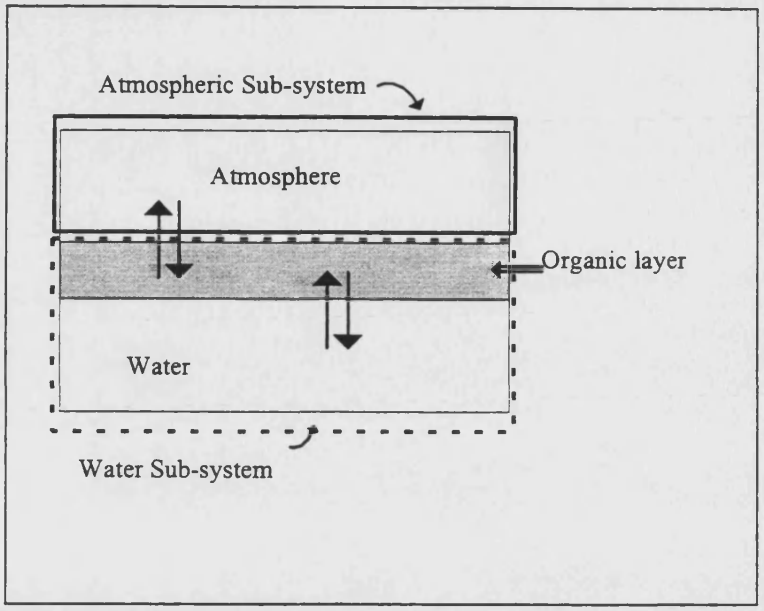

Figure 3.5 The distribution of a third phase between two sub-systems

Similar situations occur with the solid deposits on the bed of a water body and also with a soil surface which is exposed to the atmosphere.

Once the boundaries for the models have been defined the next stage is to identify the physical and chemical properties of the chemicals which dictate their movement in the environment. Section 3.4.2 examines several existing models and their limitations and briefly introduces the equilibrium model which was finally developed.

3.4.2 Development of models

Several very detailed models have been developed including those by Mackay (1979) and Neely (1980). There are three levels to the Mackay compartmental models with each successive level becoming more complex. They are described as compartmental models because they consider the transport of chemicals within and between discrete compartments. The three compartments which are considered in the first level models are the atmosphere, the water and the bottom sediments.

The first level models use a steady state mass balance, Henry's law, soil absorption data and also rate constants for dissipation in order to estimate environmental concentrations. The equations are derived assuming first order kinetics for the dissipation reactions which comprise the sum of all the possible reactions that can

occur in each sub-system. For the atmosphere the minimum data required is for advection (the rate at which the material moves out of the atmospheric compartment) with extra information on photodegradation being incorporated if available. The water sub-system again requires data on advection, but also uses rates for photolysis, microbial action and hydrolysis. The sediment system is assumed to be stationary and so advection is not considered although all other degradation reactions need to be included.

The second level models incorporate more kinetic analysis and take a more dynamic approach. These models have been used to track the behaviour of chemicals throughout a given system e.g. to study the rate of removal of particular chemicals from an ecologically sensitive area. The third level models build further on this approach by incorporating more site-specific parameters including temperature, salinity, flow and turbulence and surface area so that a particular area of interest can be studied.

The Mackay models utilise a wide range of dissipation data which is sometimes unavailable or conflicting. They are also predominantly used for determining environmental concentrations. This means that they have to be reasonably complex and can require large amounts of kinetic data. When determining the fractional distribution of a chemical in the environmental sub-systems the same accuracy is not required and therefore there is no need to utilise such complex models. Thus it was decided to develop a separate equilibrium model which does not include removal mechanisms. A measure of the degradation and dissipation of the pollutants would be included separately as a scaling factor within EniVal as outlined previously in Section 3.3.3.

In this current study two attempts have been made to develop a suitable equilibrium model. The first attempt was based on comparing the probabilities that chemicals would move from one medium to another. This movement was described using several parameters which were functions of the chemical's physical and chemical properties. In order to provide a useful analysis of the distribution, the parameters had to be scaled so that they were all considered over the same range.

All of the pollutant movements were described using the values of the air-water partition coefficient (K_W) and the soil adsorption constant (K_{OC}). The major problem with this method was that maximum and minimum values had to be defined for each of the systems in order to scale the parameters. The model became extremely complex when it came to defining these limits for the single parameters K_W and K_{OC} and appeared even more complex for the soil-air system. After extensive research it was decided to abandon this model and consider a different approach which would not involve this problem of limits. A more detailed explanation of the development of the first model is provided in Appendix B.

A second and simpler model has been developed and implemented which utilises the concept of an environmental mass balance and long-term equilibrium relationships for pollutants. This model incorporates information on the overall volumes of each of the three sub-systems in the environment as defined further in Section 3.4.3.

3.4.3 Quantifying the boundaries

Each of the three sub-systems (atmosphere, water and soil) need to be defined so that an effective analysis can be made. The volumes were finally chosen by comparing the distribution results given by the model with quantitative assessments of the long-term fate of chemicals in the environment. The assessments were made using analyses of descriptive passages from several sources (Howard 1989, 1990).

It was determined that the atmospheric system would include all of the matter in the atmosphere up to an altitude of 50 km including air, suspended particulates, volatile chemicals and water vapour. The water sub-system was defined so as to include all of the surface and ground water on the Earth, except for what is considered to be 'soil water'. This includes all of the water in the oceans and seas, rivers and lakes and also any material which is floating on the water, such as a separate layer of an insoluble organic chemical.

The water which makes up the polar ice caps is considered in the soil system as it is a separate solid phase, the majority of which covers land. The soil sub-system was selected to include all the organic and inorganic material to a depth of 1 metre given

a 30% coverage of the Earth's surface, plus the air and water which is trapped within the soil. The volume fractions of the three sub-systems (a, w and s) were calculated using these approximate volumes for the sub-systems over the entire earth. The volume fractions of each sub-system are displayed in Table 3.1 and the full calculations of the sub-system volumes are provided in Appendix C.

Table 3.1 Volume Fractions of the Environment Sub-systems

Sub-system	Volume fraction of sub-system
Atmosphere	0.95
Water	0.05
Soil	4.8×10^{-6}
Total	1

As can be seen in the table the atmosphere is by far the largest sub-system, followed by the water and then the soil.

3.4.4 The equilibrium fate model

To develop the model for the analysis of the fate of the chemical pollutants a simple mass balance was performed around the system defined in Figure 3.4. The mass balance equation states that the total quantity of the pollutant in the environment is equal to the sum of the quantities in the atmosphere, the water and the soil. The equation is as follows:

$$V_T c_T = V_A c_A + V_W c_W + V_S c_S \qquad (3.1)$$

where:

V_i is the volume of system i (m^3); and

c_j is the concentration of pollutant j (moles/ m^3);

and the subscripts are:

T total system;

A the atmospheric system;

W the water system; and

S the soil system.

This can be simplified to

$$V_T c_T = V_T(a\,c_A + w\,c_W + s\,c_S) \qquad (3.2)$$

where:

a is the atmosphere volume fraction;

w is the water volume fraction; and

s is the soil volume fraction.

Which provides the final mass balance:

$$c_T = a\,c_A + w\,c_W + s\,c_S \qquad (3.3)$$

The other expressions which are necessary for this model are the equilibrium equations for the air-water and the soil-water sub-systems. These are Henry's Law and the linear soil adsorption isotherm.

$$c_W = K_w c_A \qquad (3.4)$$

$$c_S = d\,f_{oc}\,K_{oc}\,c_W \qquad (3.5)$$

where

d is the soil density; and

f_{oc} is the fraction of organic carbon in the soil.

These three equations (3.3) to (3.5) can be solved to yield the fraction of the pollutant in each sub-system as follows:

Fraction of the pollutant in the atmosphere: $$F_a = \frac{a}{\left(a + wK_w + sdf_{oc}K_{oc}K_w\right)} \qquad (3.6)$$

Fraction of the pollutant in the soil: $$F_s = \frac{sdf_{oc}K_{oc}}{\left(\frac{a}{K_w} + w + sdf_{oc}K_{oc}\right)} \qquad (3.7)$$

Fraction of the pollutant in the water:

$$F_w = \frac{w}{\left(\frac{a}{K_w} + w + sdf_{oc}K_{oc}\right)} \qquad (3.8)$$

The model relies on the availability of the parameters which describe the distribution of chemicals throughout the environment namely the values of K_W and K_{OC}. There are two different methods for obtaining these values, the first of which is by experimentation. Both of the parameters can be derived by conducting batch experiments on air-water systems and soil-water systems respectively and are cited in a wide range of literature sources. Experimental values for K_W, which are the inverse of the Henry's Law constants H, are published in many books such as Howard (1989, 1990) and Mackay, Shiu and Ma (1992) and in a large number of scientific journal articles e.g. Yaws, Yang and Pan (1991). The values can also be obtained by using correlations which have been derived both analytically and theoretically.

The second method is by utilising correlations developed for the estimation of difficult to measure or widely used parameters. The K_W values are generally derived from equations which have been developed from thermodynamic principles. A good summary of these methods can be found in the paper "Henry's Law Constants for 362 Organic Chemicals" (Yaws et al, 1991). Professor Yaws has also developed a computer program which calculates these constants based on the thermodynamic principles and the vapour-liquid equilibrium data.

Soil adsorption constant values can also be estimated using a number of correlations which have been derived by fitting experimental data to logarithmic expressions. The value of K_{OC} can be estimated using correlations based on the chemical's solubility (S), the octanol-water partition coefficient (K_{OW}) or the bioconcentration factor (BCF). The correlations which are most commonly used to estimated the soil adsorption constant are shown in Table 3.2.

Table 3.2 Correlations for soil adsorption constant (Lyman et al, 1982)

Variable	Units of Variable	Correlation
Solubility (S)	ppm	$\log K_{OC} = 3.64 - 0.55 \times \log(S)$
Octanol/water partition Coefficient (K_{OW})	Dimensionless	$\log K_{OC} = 1.377 + 0.544 \times \log(K_{OW})$
Bioconcentration factor (BCF) flowing aquatic system static aquatic system	 Dimensionless Dimensionless	 $\log K_{OC} = 1.886 + 0.681 \times \log(BCF)$ $\log K_{OC} = 1.963 + 0.681 \times \log(BCF)$

There is a large variation in the values which are produced by the above correlations. Of the four equations shown in Table 3.2, the solubility and the K_{OW} equations are most often used, as the BCF is often derived from the K_{OW} using other correlations. To use the BCF to estimate K_{OC} would only compound any errors in the original relationship used to determine the BCF. The K_{OC} values which are predicted by the octanol-water partition coefficient method are often several times greater than those calculated by the solubility method. Also the values predicted by the solubility method usually tend to be a closer match to the experimentally derived values, and as such the solubility correlation is generally the most accurate. It should be noted however, that where experimental values are available, they should be used in preference to any derived from correlations.

3.4.5 Testing the distribution model

The model was tested using a selection of 44 organic chemicals which are commonly used as solvents in the chemical industry. Most of the data for the physical properties of these chemicals was obtained from the *Handbook of Environmental Fate and Exposure Data* (Howard, 1990). Henry's Law constants were available for all of the chemicals, but some experimental values for K_{OC} could not be obtained. In these cases, the correlation which incorporated the solubility of the chemical was used to estimate a value for the adsorption constant.

Testing was performed by using a spreadsheet containing all of the information pertaining to each chemical and the definition of the sub-systems. The fractions of each chemical which were distributed to each sub-system at equilibrium (F_a, F_W and F_S) were calculated from equations (3.6) to (3.8) and the figures were then

compared with a set of assumed values which were determined by analysing a series of descriptive passages in Howard (1990) dealing with the long-term terrestrial, aquatic and atmospheric fate of chemicals.

It is possible that significant errors can be introduced into the testing of the model through misinterpretation of this information. Hence, the passages were analysed by the author and another chemical engineer in order to determine a final set of assumed values. These values were then compared with those calculated by the model using an overall error tolerance of 15% in each medium. From the original survey, the model agreed with the assumed values for 73% of the chemicals. The results for the chemicals tested are provided in Appendix D.

3.4.6 Model error

There are several major sources of error in the model. One arises from uncertainty in the chemical and physical data required to estimate the long-term term fate of the chemicals. Analytically derived values for the distribution parameters are often not as accurate as those derived experimentally. This is clearly illustrated by the extreme variations observed in the values produced using the correlations shown in Table 3.2 for estimating K_{OC}.

Another possible source of error is the estimation of the volumes used for each of the sub-systems of the environment. Such errors could arise as a result of the assumed values including the height of the atmosphere and the depth, coverage, density and fraction of organic carbon of the soil. There will also be errors introduced by transposing the volumes of the Earth to an application at a specific site.

The assumption that the separate phases such as heavy particulates and insoluble organics are included within one sub-system also introduces errors. The model would be much more complicated if it considered the interactions between four or five sub-systems instead of the three selected.

3.5 Inorganic models

The model which was developed to assess the behaviour of organic chemicals could not be extended to inorganic pollutants since the equilibrium distribution relationships are quite different. The behaviour of inorganic pollutants is much harder to quantify because unlike for organic chemicals there is no uniform pattern which is followed by different types of inorganics. Thus in order to determine the long-term distribution of inorganic chemicals a set of rules based on the behaviour of key pollutants was used.

Inorganic chemicals are categorised into five basic groups as shown in Table 3.3 according to common physical and chemical characteristics. The distribution behaviour of chemicals within these groups is then defined using the solubility of the chemical in each class of pollutant. The solubility-based rules for these five inorganic groups are shown in Table 3.4 to Table 3.7. In all of these tables the solubility (S) is measured at 20 °C and the fractions of the chemical in the atmosphere, water and soil are denoted by F_A, F_W and F_S respectively.

Table 3.3 Inorganic Pollutant Classes

Group	Class
1	Heavy metal based compounds
2	Solids
3	Aqueous solutions/liquids
4	Gases
5	Particulates

3.5.1 Heavy metals

Heavy metals are often discharged from processes after being introduced as trace impurities in raw materials or as catalysts. In the environment they commonly exist in one of four possible forms:

- aqueous solutions of metal cations;
- metal aerosols in the atmosphere;
- metal vapours in the atmosphere; and
- heavy metal based compounds in sediments and soils.

Of these four forms the compounds present in the soils are the most common. For long-term considerations the majority of heavy metals will remain in the soil. Caughtrey, Martin and Unsworth (1987) identified that "if metals are dumped to the land then they will most likely remain there with minimal leaching or vaporisation" and that subsoils "have a potentially large capacity to resorb any metals which percolate from the top soil". From this it was decided that in the long term heavy metals would only be considered in the soil sub-system as shown in Table 3.4.

Table 3.4 Solubility model for heavy metals

F_A	F_W	F_S	Solubility (wt %)
0.0	0.0	1.0	For all heavy metals

3.5.2 Solids and aqueous solutions

For inorganic solids and aqueous solutions of inorganic solids there are no definite boundaries for classifying their distribution between the soil and the water. The limits which are used in the model are derived by examining the solubilities of various inorganic solids and their usual behavioural patterns. Solids such as Sodium hydroxide ($S \approx 50$ wt% at 20 °C) and sodium chloride ($S = 36$ wt% at 20 °C) both readily dissolve to form aqueous solutions. However materials such as calcium sulphate or gypsum ($S = 0.22$ wt% at 20 °C) which is commonly used for producing plaster of Paris and alumina ($S = 1 \times 10^{-4}$ wt% at 20 °C) will form a suspension in water and will settle if given sufficient time. Thus an intermediate aqueous solubility of 1 wt% (at 20 °C) was chosen to differentiate between the distribution of inorganic solids between the water and the soil. The same rules as shown in Table 3.5 are applied for those solids which are discharged in aqueous solutions.

Table 3.5 Solubility model for inorganic solids and aqueous solutions

F_A	F_W	F_S	Solubility (wt %)
0.0	0.0	1.0	$S < 1$
0.0	1.0	0.0	$S \geq 1$

3.5.3 Gases and aqueous solutions

Similarly for inorganic gases there are no common relationships for their distribution between the water phase and the atmosphere. However as there is a wide range of

solubility data available for inorganic gases an intermediate stage is included to represent a partial distribution between both the water and the air. Some gases such as hydrogen (S = 0.002 wt% at 20 °C) and nitrogen (S = 0.002 wt% at 20 °C) will normally be present in the atmospheric sub-system only. Others such as carbon dioxide (S = 0.16 wt% at 20 °C) and chlorine (S = 0.81 wt% at 20 °C) will normally partially dissolve to form aqueous solutions while many gases such as hydrogen chloride (S = 72 wt% at 20 °C) readily dissolve and will usually exist as aqueous solutions. The gases that readily dissolve will be very susceptible to scavenging from the atmosphere by rain. It has been assumed that the adsorption of gases by soils in negligible compared to the transport via aqueous solution. From this data the distributions for inorganic gases between the water and the atmosphere were defined as shown in Table 3.6.

Table 3.6 Solubility model for inorganic gases and aqueous solutions

F_A	F_W	F_S	Solubility (wt %)
1.0	0.0	0.0	$S < 0.1$
0.7	0.3	0.0	$10 > S \geq 0.1$
0.0	1.0	0.0	$S \geq 10$

3.5.4 Particulates

Many chemical operations, particularly those which include combustion processes produce particulates. Particulates consist of small particles of inorganic matter predominantly composed of carbon which range from smoke (0.01 - 1 μm) through dust (> 1 μm) up to fine material (10 - 100 μm). For particles with a diameter greater than 2 μm gravitational settling is a significant removal mechanism and those with diameters greater than 10 μm will settle rapidly by gravity (Hemond and Fechner, 1994). Very few processes will quantitatively measure particulates less than 10 μm in size and smoke discharges are rarely reported or quantified. Thus the remainder of the particulates will eventually settle and therefore will only be considered in the soil sub-system in the long term as shown in Table 3.7.

Table 3.7 Solubility model for particulates

F_A	F_W	F_S	Solubility (wt %)
0.0	0.0	1.0	For all particulates

3.6 Summary

This chapter has examined the scope for the analysis of environmental impact and identified the boundaries with respect to both temporal and spatial limits. A series of models have been presented which estimate the long-term equilibrium fate of both organic and inorganic chemicals in the environment. The tree configuration which provides the structural support for the many effects which need to be considered in the impact analysis has been defined from the overall impact value down to the fifth level representing damage, modification and persistence.

The next chapter continues with the definition of the tree by filling in the last two levels which contain all of the individual physical and chemical parameters which are used to quantify the effects represented in the upper levels of the tree. After defining the structure and contents of the tree working from the top level to the bottom the combination of all of the raw data in the lowest level then needs to be considered by working in reverse from the lowest levels to the top. This progression is presented in Chapter 5 which is followed by the presentation in Chapter 6 of the chemical processes used to test EniVal.

Chapter 4

Identification of impact parameters

The two lowest levels (levels 6 and 7) of EniVal contain all of the raw data used to represent the environmental impact of a given chemical. Level 6 identifies the effects which are being quantified and level 7 contains the parameters which are used to represent each of these effects. As mentioned in Chapter 3 the effects of exposure to a given chemical are dependent on two major factors:

- the location; and
- the timescale.

Thus in order to perform a thorough analysis of environmental impact these effects need to be considered separately using different parameters where necessary. This chapter identifies the major effects which are considered in each environmental medium and the parameters which are used to quantify them for both the long-term and short-term assessments. The parameters were chosen to reflect the likelihood of one particular chemical contributing to an environmental effect relative to another chemical and they were selected as overall indicators rather than measures of specific effects.

4.1 Short-term impact

This section presents the lowest levels of EniVal for the determination of the short-term impact of a pollutant. Although the three impact branches (damage, modification and persistence) are incorporated throughout the analysis of the whole environment, many of the parameters which are used to indicate each of the relevant effects vary between media. The damage branch of the tree always has two sub-branches representing toxicity and hazards and the hazards are always assessed using two further sub-branches for flammability and explosivity for all media. In the following sections the parameters are described fully the first time that they are presented and then mentioned briefly with each successive usage.

4.1.1 Atmospheric factors

The lowest four levels of the short-term atmospheric impact tree are illustrated in Figure 4.1.

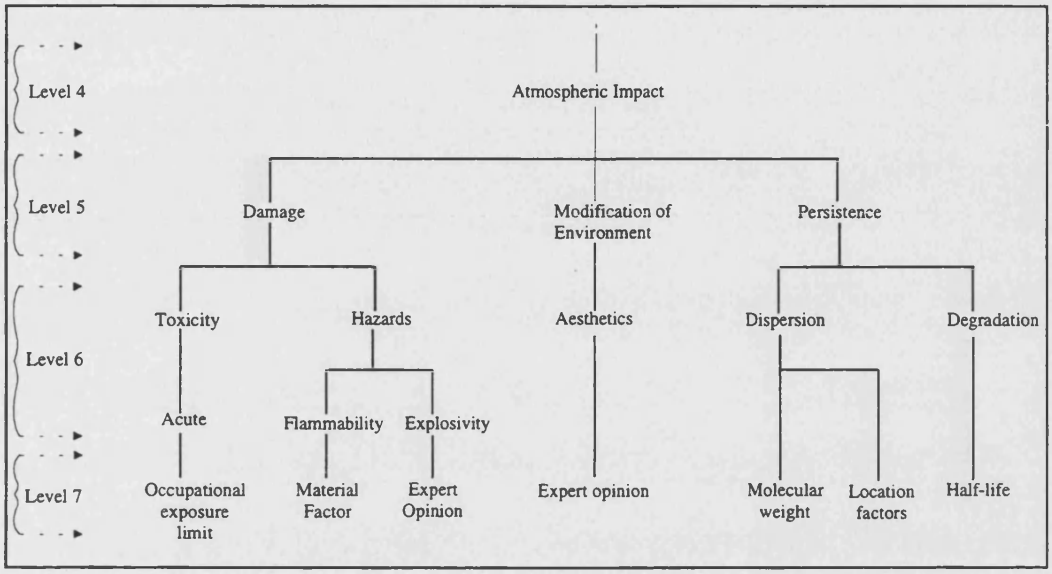

Figure 4.1 Representation of short-term atmospheric impact

The damage branch for the consideration of the short-term impact of a chemical on the atmospheric sub-system quantifies both the toxicity and the hazards associated with that chemical as shown in Figure 4.1.

Toxicity

For humans and other animals the most likely method of exposure to a given chemical in the atmosphere is via inhalation. The parameter which has been selected to represent the relative acute toxicity of a given chemical in the atmospheric environment is the Occupational Exposure Limit (OEL). The OEL may be either an Occupational Exposure Standard (OES) or a Maximum Exposure Limit (MEL). The OES and MEL values are defined by the Health and Safety Executive (Health and Safety Executive, 1994). The OES is the "threshold above which there may be evidence of significant effects on health but below which, on existing knowledge, there are thought to be no adverse effects" based on a working lifetime exposure with 8hr/day exposure. The MEL is generally used instead of the OES when there are "serious implications for the health of workers exposed to the substance", including "both the risk of serious health effects to a small population of workers and

the risk of relatively minor health effects to a large population". The OEL may not be the best measure to use but there is a wide range of data available which makes it practical for this type of analysis.

Hazards

The flammability of a chemical can be assessed using parameters such as the flashpoint and the autoignition temperature. The Dow Chemical Company's Fire and Explosion Index (FEI) (Dow Chemical Company, 1987) utilises a parameter called the Material Factor (MF) which is representative of the flammability and reactivity of a chemical. It is calculated using heats of combustion as shown in equation (4.1) (Coulson and Richardson, 1983).

$$MF = -\Delta H_c \times \frac{4.3\times10^{-4}}{MW} \qquad (4.1)$$

where:

$-\Delta H_c$ is the standard heat of combustion at 25°C [kJ/kmol]; and

MW is the molecular weight.

Some chemicals exhibit a tendency to detonate or explode under certain process conditions. The user's opinion or expert opinion if available is used to assess the two major categories of this type of behaviour which are considered in the explosivity factor. These are:

1. materials which demonstrate explosive decomposition; and
2. chemicals which may detonate under process conditions if protective control systems fail.

Aesthetics

Each of the three environmental media has a parameter which provides a measure of the potential impact resulting from any detrimental visual or other sensory effects in the surrounding environment. While the overall concept of the parameter remains constant the scoring systems vary according to the likely effects on each medium as presented in section 4.3.2. The two main effects which are studied are visual impact and problems due to odour.

Dispersion

The dispersion of a chemical within each sub-system of the environment will have an effect on the extent of the chemical's impact. The movement of a chemical in the atmosphere is mainly dependent on local atmospheric conditions represented by the location factors described in section 4.3.3. The molecular weight of a gaseous chemical is important for high concentration releases where the density of the release is significantly affected by the concentration of the pollutant. While EniVal currently utilises the molecular weight, a more realistic parameter may need to be defined for future investigations.

Degradation

The rate of degradation of chemicals is assessed using typical values for their half-lives in the environment. Data for the half-lives in each of the media have been obtained from a variety of reference sources including Mackay et al (1992), Howard et al (1991) and the US EPA (1979). There is also a range of databases available such as those provided by the Syracuse Research Corporation (SRC) Environmental Fate Data Bases (EFDB) and the DATALOG, CHEMFATE, BIOLOG and BIODEG files (LaGrega, Buckingham and Evans, 1994). The half-life data contained in these sources considers the maximum and minimum rates of the most significant degradation processes in each sub-system in order to provide a comprehensive investigation of the behaviour of the chemicals. Some of the more common routes of degradation in each of the sub-systems are listed Table 4.1.

Table 4.1 Common routes of degradation for chemicals in the environment

Medium	Routes of Degradation		
Atmosphere	Photo-oxidation	Photolysis	Hydroxyl radical reaction
Water	Biological decomposition	Photolysis	Hydrolysis
Soil	Aerobic biodegradation	Anaerobic biodegradation	Hydrolysis

4.1.2 Water factors

Figure 4.2 shows the parameters which are used to quantify the short-term impact of a given chemical on the water sub-system of the environment.

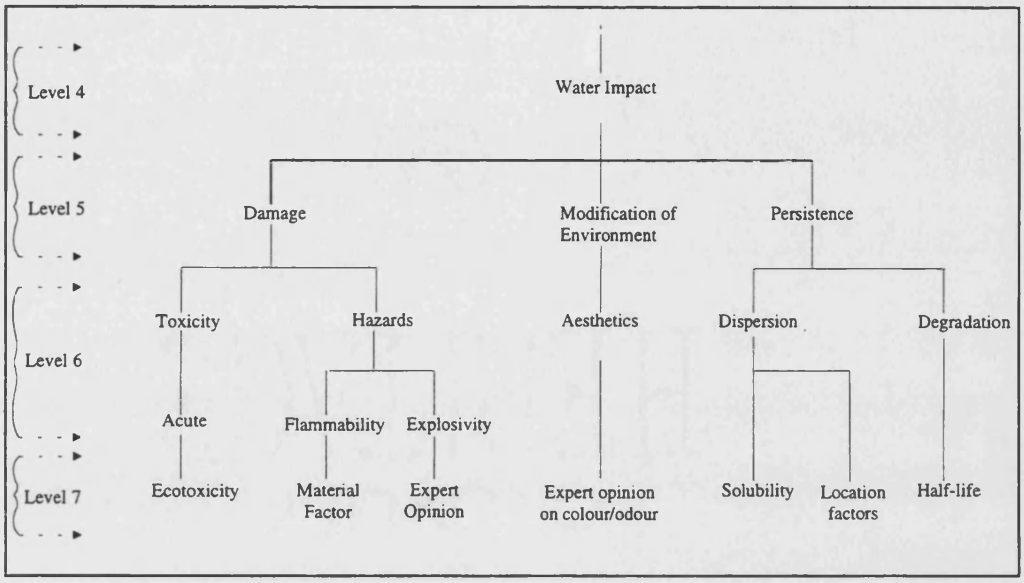

Figure 4.2 Representation of short-term water impact

Toxicity

For an aquatic system the main exposure routes are via ingestion and absorption. Kaiser and Palabrica (1991) presented a technique called the Microtox™ test which involves assessing the toxicity of organic chemicals using the luminescent marine bacterium *Photobacterium phosphoreum*. This technique is identified as being a "simple, fast and comparatively inexpensive alternative to *in-vivo* bioassays with higher organisms". This means that the ecotoxicity (EC_{50}) which is generated by this test can be used to represent the toxicity of a given chemical to the surrounding ecology. Thus the acute toxicity of pollutants in the water system is assessed using a scoring system based on the EC_{50}.

Hazards

The flammability and explosivity of a chemical in the water system is assessed using the material factor and the expert judgement respectively as discussed in section 4.1.1.

Aesthetics

The modification branch for the water system only incorporates a measure of the aesthetic impact of a chemical. As for the atmospheric system this parameter provides a measure of the impact of any unsightly coloured discharges or unpleasant odours which may accompany the release of a chemical.

Dispersion and degradation

In an aquatic system the probability of a chemical remaining in solution can be estimated using its solubility. If a chemical remains in aqueous solution then it is more likely to be transferred within the water sub-system. As for the atmospheric system there are several local factors which dictate the extent to which these chemicals will be dispersed in a given aquatic environment. The degradation of a chemical in the water system is assessed using the half-life for that chemical in an aqueous environment as described in section 4.1.1.

4.1.3 Soil factors

Figure 4.3 shows that for the assessment of the fifth level of EniVal for the soil system the impact is described using the damage and the modification branches only, due to the assumption that in the short-term chemicals are will not disperse readily.

Toxicity

The acute toxicity of a chemical which is discharged to the soil is measured using the EC_{50} the same as for the water system because exposure is more likely to occur through ingestion or absorption than via inhalation.

Hazards and aesthetics

The hazards branch is the same as for the other environmental media with the material factor and explosivity while the modification branch incorporates a measure of the potential aesthetic impact of a chemical as described in sections 4.1.1 and 4.1.2.

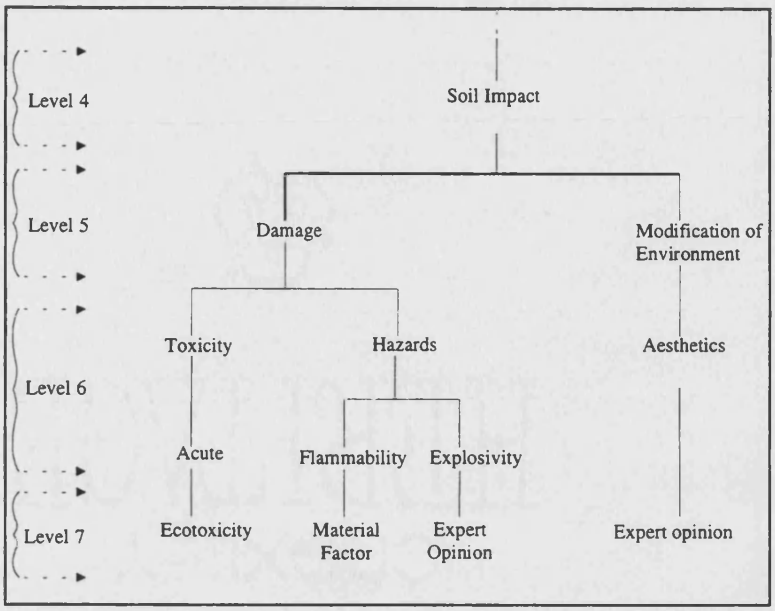

Figure 4.3 Representation of short-term soil impact

4.2 Long-term Impact

Section 4.1 has presented the parameters used to assess the short-term effects of a chemical on the environment. This section now discusses the assessment of the long-term effects of a chemical. As for the short-term analyses the three impact branches (damage, modification and persistence) appear throughout the assessment and the parameters which are indicative of the relevant effects vary between the media.

4.2.1 Atmospheric factors

Figure 4.4 shows the impact branch used to assess the long-term impact of a chemical on the atmospheric environment.

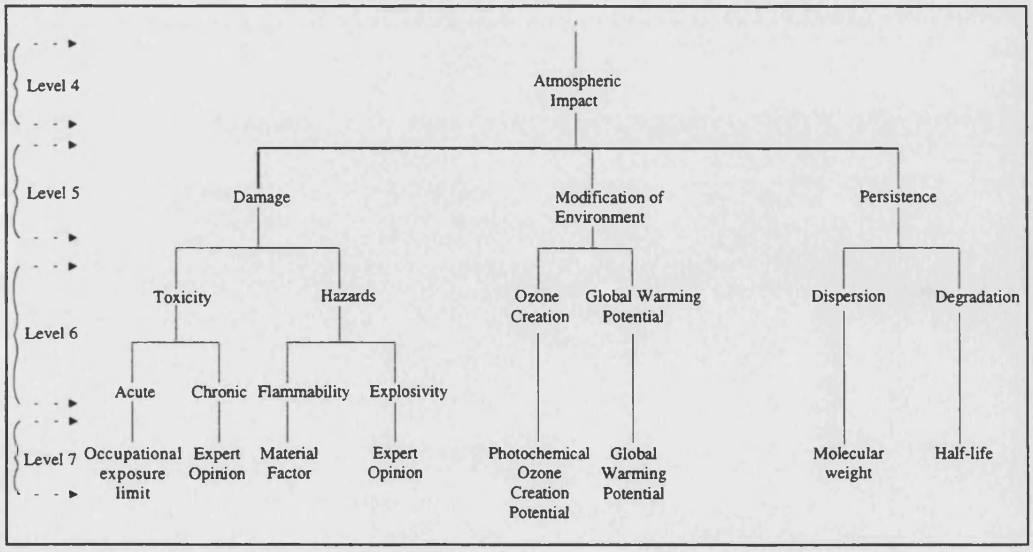

Figure 4.4 Representation of long-term atmospheric impact

Toxicity

As part of the assessment of the long-term impact of a chemical, chronic as well as acute toxic effects must be considered. In this case the acute toxicity is assessed using the OEL as for the short-term analysis presented in section 4.1.1. However, the chronic toxicity of a chemical is a very difficult characteristic to quantify as it often depends on a number of variable factors. One of these factors is the target organ which is the organ that the chemical attacks in the victim. This organ varies for each chemical, between individuals and between species. It can also vary depending on the level of the substance present.

Two different methods were investigated which could be used for quantifying the chronic toxicity of chemicals of which the most promising was the Reference Dose (RfD) which was developed by the US EPA (1979). The RfD is the dose below which the chemical should have no adverse health effects. It has been developed for different exposure routes (e.g. oral and inhalation) and also different exposure times (e.g. chronic and acute). Although the RfD could be used to provide all the information necessary for this study of the chronic toxicity of chemicals there appears to be little data available at present. The samples of the Integrated Risk Information System (IRIS) database provided in LaGrega et al (1994) show that for the majority of chemicals the data do not exist.

Until sufficient reliable data can be obtained for the RfD, it was decided that EniVal would assess the chronic toxicity of each chemical using a composite of three parameters:

- the logarithm of the n-octanol/water partition coefficient - $\log(K_{ow})$;
- the potential for the chemical to form toxic metabolites upon degradation; and
- a measure of the detrimental effect on the reproductivity of the species being studied or a measure of the carcinogenicity of the chemical if the reproductivity data is not available.

The combination of these three parameters is discussed further in section 4.3.1.

Hazards

The flammability and explosivity of a chemical in the water system is assessed using the material factor and the expert judgement respectively as discussed in section 4.1.1.

For the long-term modification of the atmospheric environment there are two major issues which have been highlighted in this study and which are shown in the modification branch of the tree in Figure 4.4. These are:

- photochemical ozone creation; and
- global warming potential.

Ozone creation

Ozone is produced in the troposphere by the action of sunlight on hydrocarbons and oxides of nitrogen. While stratospheric ozone plays a positive role in shielding the Earth from ultraviolet light, ozone in the lower atmosphere is a highly reactive pollutant which can have damaging effects on human health, vegetation and animals. The Photochemical Ozone Creation Potential (POCP) which measures the change in photochemical ozone production due to a change in emission of a particular chemical has been defined by Derwent and Jenkin (1991) and is utilised in the modification branch for the atmospheric system. The POCP is also used in the HMIP (1994b) assessment of the BPEO and in the Eco-indicator 95 (Goedkoop, 1995) as discussed previously in Chapter 2. The production of ozone in the lower atmosphere may continue for several days through a cycle in which production alternates with day-time and night-time. Although the ozone may degrade within a day of being created, more ozone is often being formed during and after this period. Thus the problem of ozone creation is considered as a long-term environmental modification issue.

Ozone depletion in the stratosphere is also a major problem and is mainly due to the action of chlorofluorocarbons and other similar chemicals. These chemicals have now been banned from commercial production and so the issue is no longer as relevant to the current operating processes. Pearce (1996) recently hypothesised that "after 10 years of effort to ban the offending chemicals, this year could be the first in

which the (ozone) hole begins to fill again". On this basis, ozone depletion is not included in this assessment.

Global warming

The existence of the phenomenon of 'global warming' is yet to be scientifically proven but it is known that carbon dioxide and other gaseous pollutants do effect the atmosphere. Whether or not the average temperature of the Earth is increasing due to the presence of greenhouse gases is unknown, but 'global warming' is still an issue of great concern to both the public and the scientific community. This fact is enough to justify the inclusion of a Global Warming Potential (GWP) in the consideration of the long-term atmospheric impact of a particular chemical. The concept of the GWP was presented in a consultation document prepared by HMIP (1994b) and is defined as the "warming contribution of each gas relative to an equal weight of carbon dioxide over a period of 100 years".

Dispersion and degradation

The persistence branch for the tree is the same as that for the short-term analysis presented in section 4.1.1 without the location factors for the dispersion. These location factors are not included in the long-term assessment because the dispersion is no longer considered on a local scale.

4.2.2 Water factors

The long-term impact of a chemical on the water sub-system is assessed using the branches of the impact tree which are shown in Figure 4.5.

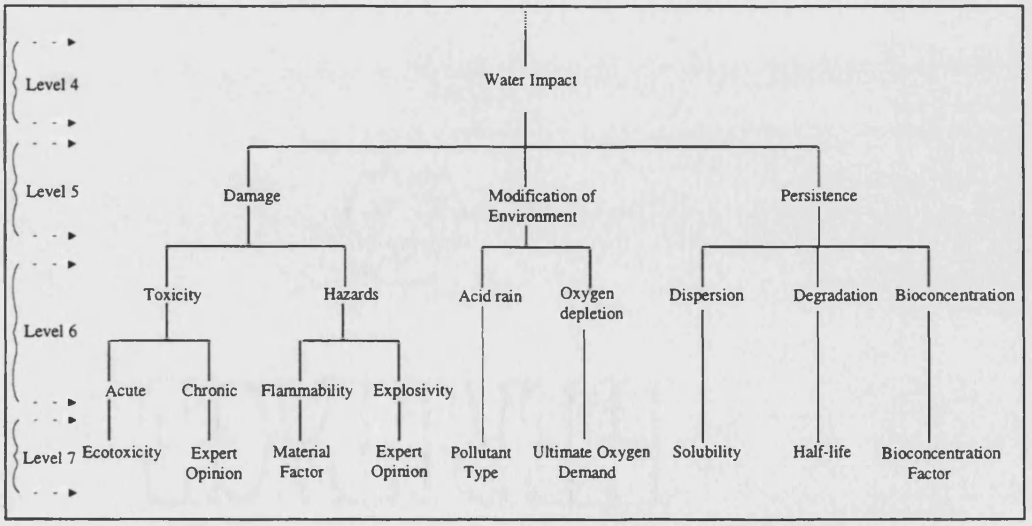

Figure 4.5 Representation of long-term water impact

Toxicity and hazards

The parameter used to assess the acute toxicity of a pollutant is the EC_{50} the same as for the short-term analysis and the chronic toxicity is quantified using the three parameters presented in section 4.2.1. The hazards are assessed using the material factor and the explosivity as for the short-term analysis.

Oxygen depletion

Long-term modification of the aquatic environment has been accounted for by assessing the oxygen demand created by liquid effluents. Oxygen demand is usually assessed by measuring the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD) in the receiving water-body. Another means of assessment is the ultimate oxygen demand (UOD) which can be determined experimentally over a 90 day period (Coulson and Richardson, 1983). The UOD can also be estimated by assuming complete oxidation of the carbon present to carbon dioxide and the nitrogen to nitrate. The formula for calculating the UOD is given in equation (4.2):

$$UOD = 2.67 \times C + 4.57 \times N \qquad \textbf{(4.2)}$$

where:

C is the concentration of carbon in ppm; and

N is the concentration of nitrogen in ppm.

The formula shown in equation (4.2) cannot be used directly in this work as EniVal was designed so that it would not utilise any environmental concentration data. Thus an alternative definition of UOD has been proposed where C and N are the number of carbon and nitrogen atoms respectively in one molecule of the chemical. Unlike the BOD, COD and the traditional UOD this parameter does not require any measurements of concentrations in the environment.

Acid rain

There are no common parameters which can be used to determine the relative contribution that a chemical will make to the formation of acid rain. Instead this contribution has been assessed using expert opinion based on the nature of the

chemicals being studied as described in more detail in section 4.3.2. The acid rain parameter appears in the water system due to the high soliubility of SO_2 and NO_x.

Dispersion, degradation and bioconcentration

The persistence branch of the tree utilises the solubility and half-life to measure the dispersion and degradation of a chemical in a water system as for the short-term assessment. However in the long-term, bioconcentration must also be assessed. Bioconcentration is the degree to which a chemical residue will accumulate in aquatic organisms.

In the consultation document on the selection of the Best Practicable Environmental Option produced by HMIP (1994b) it was recommended that the bioconcentration of chemicals only be considered in the water environment, not in the atmosphere or the soil. The reason stated for this was that it is considered unlikely that highly volatile substances will be readily accumulated. Values for the BCF as defined in equation (4.3) have been obtained from literature sources such as Howard (1989, 1990).

$$\text{BCF} = \frac{\text{Concentration of chemical at equilibrium in organism (wet weight)}}{\text{Mean concentration of chemical in water}} \qquad \textbf{(4.3)}$$

4.2.3 Soil factors

The branch for the analysis of the soil sub-system shown in Figure 4.6 is the same as that for the water system with the exception of the modification branch and dispersion in the persistence branch.

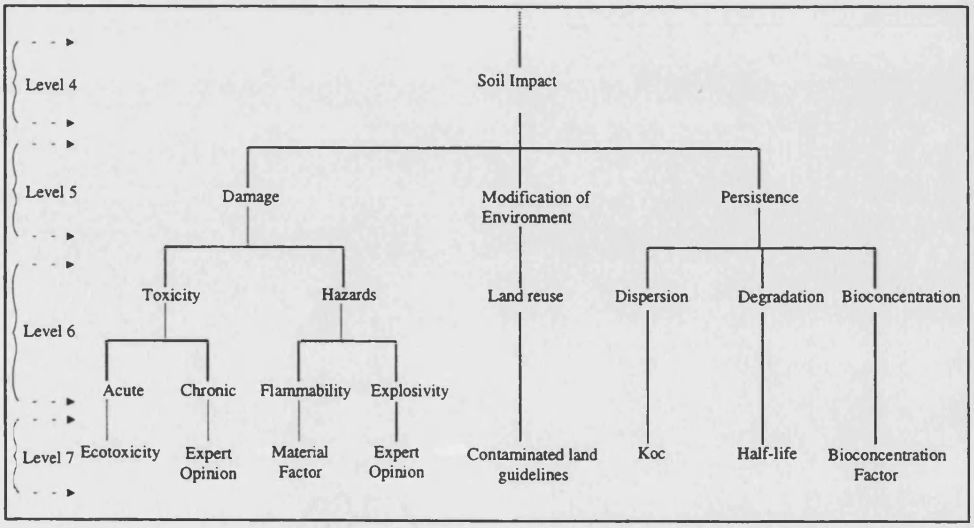

Figure 4.6 Representation of long-term soil impact

Land reuse

The main long-term impact that has been identified for the discharge of a pollutant to the soil is the restriction of the future use of that area of land. The remediation of this contamination is often a costly and time-consuming problem for any developer and it may considerably reduce the value of the land. The Inter-departmental Committee on the Redevelopment of Contaminated Land (ICRCL) (1987) has produced guidelines on the assessment and redevelopment of contaminated land which use "trigger concentrations" to determine whether or not remediation is required. These data from these "trigger concentrations" have been adapted to identify those pollutants which can cause significant problems when discharged to land as described fully in section 4.3.2.

Dispersion

Unlike in the short-term investigation the analysis of the long-term impact of a chemical on the soil system includes a measure of dispersion (K_{oc}) because the transportation processes in the soil environment, whilst slow are finite. In the short-term a chemical is unlikely to be transported throughout the soil, however in the longer term this transport may be more significant. The degradation and bioconcentration are assessed using the same parameters as for the water system described in section 4.2.2.

4.3 Scoring systems

All of the parameters which have been identified in sections 4.1 and 4.2 as being crucial to the assessment of environmental impact must be quantified for each pollutant. As previously highlighted in Chapter 1, one of the most important properties of EniVal is that it is based purely on the mass emissions of the chemicals and therefore does not depend on or require the concentrations of the pollutants in the environment. In order to quantify the impact of chemicals, a series of scoring systems has been developed which is based solely on the properties of chemicals and not their concentrations. This process is based on a ranking system whereby the relevant parameters are scored and weighted to give an overall impact.

The raw data are scaled according to how strongly a chemical exhibits the behaviour which is described by the parameter. All the parameters are graded on a scale ranging from either 0-10 or 1-10 to provide a consistent set of values for all parameters. In some cases the scoring system is based purely on a selected range of typical values such as for solubility and BCF while in others such as chronic toxicity and explosivity, the scoring system is based on a combination of scores for a number of selected indicative parameters.

4.3.1 Damage parameters

As described in sections 4.1 and 4.2 the assessment of the damage caused to the environment by a pollutant is quantified using the following range of parameter groups:

- acute toxicity parameters;
    - OEL
    - EC_{50}
- chronic toxicity parameters;
    - n-octanol/water partition coefficient
    - toxic metabolite formation
    - reproductivity/carcinogenicity.
- material factor; and
- explosivity.

Some of these parameter groups are assessed using scoring systems which combine a number of different variables. Table 4.2 illustrates the simple scoring systems for four of these parameters while the rest of the scoring systems are defined within the descriptions which follow.

Table 4.2 Damage parameters' scoring systems

Score	OEL & EC_{50} (mg/m^3)	Reproductivity concentration (mg/m^3)	Material Factor	Explosivity
0	-	-	0	Explosive decomposition
1	$> 10^4$	$> 10^5$	0^+ - 10	
2	10^3 - 10^4	10^4-10^5	10 - 15	
3	10^2 - 10^3	10^3-10^4	15 - 20	
4	10 - 10^2	10^2-10^3	20 - 25	
5	1 - 10	10^1-10^2	25 - 30	
6	10^{-1} - 1	10^0-10^1	30 - 35	Detonation
7	10^{-2} - 10^{-1}	10^{-1}-10^0	35 - 40	
8	10^{-3} - 10^{-2}	10^{-2}-10^{-1}	40 - 45	
9	10^{-4} - 10^{-3}	10^{-3}-10^{-2}	45 - 50	
10	10^{-5} - 10^{-4}	10^{-4}-10^{-3}	50 - 60	

The acute toxicity of any chemical is usually dependent on the route by which the victim is exposed to the pollutant. The three major exposure routes are via inhalation, ingestion or dermal absorption. For this study, the acute toxicity of pollutants in the atmospheric sub-system is assessed using the data for inhalation and for the water and soil sub-systems data are obtained for the other exposure routes.

The long-term occupational exposure limits as described in section 4.1.1 are used to assess the acute toxicity of chemicals in the atmospheric sub-system. The values for the OEL published in the Health and Safety Regulations (Health and Safety Executive, 1994) range between 0.00006 mg/m^3 (subtilisins - crystalline proteolytic enzymes) and 9,000 mg/m^3 (carbon dioxide). These values were taken as the extremes of the range for the scoring system. Thus all the chemicals within this range are scored according to how toxic they are relative to each other. The acute toxicity for the water and soil systems is assessed using the ecotoxicity (EC_{50}) as discussed in section 4.1.2. To maintain consistency the same range of data is used for the scoring systems for both the OEL and the EC_{50}.

As described in section 4.2.1 the chronic toxicity of a chemical is very difficult to assess given the wide range of possible effects. Thus the scoring system relies on three parameters:

- the logarithm of the n-octanol/water partition coefficient - $\log(K_{ow})$;
- the potential for the chemical to form toxic metabolites upon degradation; and

- a measure of the detrimental effect on the reproductivity of the species being studied or the potential carcinogenicity.

The distribution of a chemical between an aqueous system and the fatty lipids of a living organism can be predicted using the logarithm of the n-octanol/water partition coefficient ($\log(K_{ow})$). The greater the value of $\log(K_{ow})$ the more likely the chemical is to be absorbed into the organism's tissues. Chemicals with a $\log(K_{ow})$ value of greater than three are almost certain to bioaccumulate. The $\log(K_{ow})$ scores as shown in Table 4.3 are used as a measure of the extent of the effect. This effect is scored using the metabolite and reproductivity tests.

Table 4.3 n-Octanol/water partition coefficient scoring system

$\log(K_{ow})$	Score
<0	0.1
0-1	0.3
1-2	0.5
2-3	0.7
≥3	1

Many chemicals exhibit a secondary toxicity by producing by-products upon degradation which are more toxic than the original pollutant. This parameter is scored according to the user's opinion on a scale of 0-10 depending on the number of possible toxic metabolites which may be formed and their relative toxicity. These metabolites can be found by examining typical degradation pathways.

There are tests which may be carried out to determine the extent of the long-term effects which may result due to exposure to certain chemicals. While the limitation of the potential for a given species to reproduce is one of the most effective measures of chronic toxicity there are few data available for providing a consistent scoring system. If this data is available then the reproductivity scoring system as presented Table 4.2 should be used. However if it is not available then the carcinogenicity scoring system presented in Table 4.4 should be used in its place.

Table 4.4 Carcinogenicity classes (LaGrega et al, 1994)

Score	Class	Description
10	A	Human Carcinogen - "there is sufficient evidence from epidemiological studies to support a causal association between exposure to the agent and cancer"
8	B1	Probable human carcinogen - limited human data available
6	B2	Probable human carcinogen - sufficient evidence in animals and inadequate or no evidence in humans
4	C	Possible human carcinogens
2	D	Not classifiable as to human carcinogenicity
0	E	Evidence of non-carcinogenicity for humans.

The final score for the chronic toxicity is assessed using equation (4.4) whereby the log(Kow) score is used as a weighting factor to be multiplied by the average of the scores for the potential for the production of toxic metabolites and the reproductivity tests.

$$\text{Chronic Score} = \frac{\overline{\text{logKow}} \times \left(\overline{\text{Repro}} + \overline{\text{Metab}}\right)}{2} \qquad \textbf{(4.4)}$$

where:

$\overline{X}$ denotes the score for the parameter X;

Repro is the reproductivity parameter; and

Metab represents the potential for creating toxic metabolites on degradation

The flammability of a chemical is assessed using the Material Factor which was developed as part of the Dow Fire and Explosion Index (Dow Chemical Company, 1987). The material factor provides an indication of the magnitude of the energy released by the chemical during a fire or explosion. Its value ranges between 0 and 60 (Coulson and Richardson, 1983).

Some chemicals exhibit a tendency to detonate or explode under certain process conditions. In order to provide a quantitative measure of its explosivity, a chemical is scored according to the user's judgement on the likelihood of it behaving in either of two ways (materials which demonstrate explosive decomposition and those which may be likely to detonate under process conditions if the protective control systems fail) as shown in Table 4.2..

4.3.2 Modification parameters

The second branch of the impact tree deals with any remaining parameters which should be included to quantify a pollutant's impact on the environment that are not assessed within the damage branch. These modification parameters are:

- photochemical ozone production;
- global warming potential;
- acid rain formation;
- oxygen depletion;
- land reuse; and
- aesthetics.

The first four of these parameters are scored using the methods given in Table 4.5 and the remaining two parameters are defined in the following sections.

Table 4.5 Modification parameters scoring systems

Score	POCP	Global Warming Potential	Acid rain (type of pollutant)	UOD
0	0	0	Inactive	0
1	1 - 10	1 - 10		0^{+} - 10
2	10 - 20	10 - 100		10 - 20
3	20 - 30	10^2 - 10^3		20 - 30
4	30 - 40	10^3- 2×10^3		30 - 40
5	40 - 50	2×10^3 - 3×10^3	Secondary Pollutant	40 - 50
6	50 - 60	3×10^3 - 4×10^3		50 - 60
7	60 - 70	4×10^3 - 5×10^3		60 - 70
8	70 - 80	5×10^3 - 6×10^3		70 - 80
9	80 - 90	6×10^3 - 7×10^3		80 - 90
10	90 - 100	$> 7\times10^3$	Primary Pollutant	90 - 100+

While there is major concern over the thinning of the ozone layer in the stratosphere the production of ozone is not always desirable. In the bottom 8-13 km of the atmosphere which is known as the troposphere, the production of ozone is extremely undesirable. The POCP of a given chemical may be determined using mathematical models or through laboratory experimentation. While it is recognised that there is significant uncertainty in the POCP values themselves due to external factors influencing the level of ozone production these values are useful for classifying Volatile Organic Compounds (VOC) species according to their importance in ozone

production (LaGrega et al, 1994). The range chosen for the POCP values was 1 to 100 as shown in Table 4.5 given the range of chemicals from methyl chloroform (POCP = 2) to the alkenes (POCP = 91).

The GWP has been calculated in the HMIP BPEO document (1994b) for a limited selection of chemicals which are commonly thought to contribute most to 'global warming'. These include CO_2 (GWP = 1) and a selection of chlorofluorocarbons such as CFC12 (GWP = 7,100). The scoring system for the GWP is based on these typical values as shown in Table 4.5.

The main chemicals which are of concern when considering acid rain are those which contain nitrogen and sulphur. The UK Terrestrial Effects Group (1988) identified two classes of pollutants defined by their contribution to the formation of acid rain. Primary pollutants which include sulphur dioxide and nitrogen oxides can contribute to acid rain via either direct dry deposition or indirect wet deposition after incorporation of the chemical into rain or other carriers. Secondary pollutants which assist in the transformation of the primary pollutants to sulphate and nitrate include nitrogen dioxide (NO_2) (both a primary and secondary pollutant) and ozone (O_3). There is also a large number of chemicals which have no or minimal contribution to the problem of acid rain. These three classes of pollutants and their relative scores for their contributions to the creation of acid rain are presented in Table 4.5.

The deoxygenation of aquatic systems caused by discharges of chemicals is a very common environmental problem. One way to measure the possible impact that a chemical will have for oxygen removal is the UOD as discussed in section 4.2.2. The scoring system shown in Table 4.5 incorporates a range of values from 0 to 100. This range covers the majority of chemicals including heavy organic compounds such as many oils which may have more than 40 carbon atoms per molecule (40 C atoms gives a UOD of 106.8).

The ICRCL guidelines for contaminated land (1987) present a set of "trigger concentrations" which identify the levels at which a pollutant must be present before

remediation is required. However as yet there are no comprehensive guidelines for general chemical operations, only gas works. Also the remediation requirements and the levels that are considered to be "clean" are largely dependent on the intended future use of the land. Until further information and guidelines become available for a wide range of chemical processes the simple system as defined in Table 4.6 will be used to measure the impact of a given pollutant on future land use. This system utilises a list of common soil contaminants presented in the ICRCL guidelines and considers the number of hazards which are possible due to the presence of each of the contaminants as defined in the guidelines.

Table 4.6 Land reuse scoring system

Score	Hazards
0	Chemical not listed
5	1 hazard listed for chemical
10	2 or more hazards listed for chemical

The discharge of chemicals often creates a short-term nuisance factor in the local environment. Discharges to the atmosphere may be accompanied by unsightly clouds of smoke and steam while releases to water bodies can result in plumes of unattractive and discoloured water. While some pollutants may not contribute to the visual degradation of the environment they may have offensive odours which cause discomfort to both workers and the surrounding communities. These impacts are often overlooked in traditional impact analyses as quantification of the damage that they can cause is a very subjective process.

The scoring systems developed here analyse the impacts of releases to the atmosphere water and soil separately considering both visual and olfactory effects. The scores for the effect categories presented in Tables 4.7 to 4.9 are the maximum values possible for each of the parameters. The effect parameters are scored according to the expected severity of the impact using physical property data that is commonly available in Material Safety Data Sheets (MSDS). These scores are then summed to provide an overall aesthetic impact score ranging from 0 to 10.

Table 4.7 illustrates the five major effect categories that are considered for the aesthetic impact of a pollutant on the atmosphere. It also shows their respective weightings which provide a measure of their contribution to the overall aesthetic impact.

Visual effects due to the discharge of pollutants to a watercourse will often be very localised and will depend on local conditions. The impact is enhanced if the pollutant remains near the surface of the water where it can be seen more easily as detailed in Table 4.8. The visual effects which are assessed only consider the physical appearance of the discharge and any subsequent effects such as fish kills or dead vegetation are not considered in this parameter.

Table 4.7 Atmospheric aesthetic impact classes

Effect	Score
Particulates	1
Smoke/Steam	1
Visual flame	1
Colour	2
Smell	5

Table 4.8 Water aesthetic impact classes

Effect	Score
Flotation	2
Colour	3
Smell	5

The deposition of pollutants to land is assessed using a very similar scoring system to that utilised for the water system. Again there is a measure of how visual the deposit of a chemical will be, a measure of the impact due to its colour and an similar weighting for the olfactory effects as shown in Table 4.9.

Table 4.9 Soil aesthetic impact classes

Effect	Score
Deposition	2
Colour	3
Smell	5

Several other effects such as disturbances created by excessive noise from machinery operating within the plant, deleterious aesthetic visual effects caused by buildings and equipment on-site (e.g. large stacks) and excessive amounts of lighting can also create nuisances. However many of these problems can be minimised with good

operating practice and so these factors were not included within the scope of this assessment.

4.3.3 Persistence parameters

As mentioned previously in this chapter the parameters which are used to describe the persistence and movement of chemicals in the environment are:

- molecular weight;
- solubility;
- soil adsorption constant;
- bioconcentration factor;
- half-life; and
- location factors.

The scoring systems for the first five of these parameters are presented in Tables 4.10 and 4.11 and the details of the location factors are presented in Tables 4.12 to 4.14. A brief description of the development of these scoring systems is presented below for each parameter.

Table 4.10 Persistence parameters scoring systems

Score	Molecular weight	Solubility (ppb)	Soil Adsorption Constant - µg/g o.c. µg/ml	BCF Range	Half-Life
1	>225	< 1	1	<1	< Seconds
2	200-225	1 - 10	1 - 10	1 - 10	Seconds
3	175-200	10 - 10^2	10 - 100	10 - 10^2	Minutes
4	150-175	10^3 - 10^4	10^2 - 10^3	10^2 - 10^3	Hours
5	125-150	10^4 - 10^5	10^3 - 10^4	10^3 - 5×10^3	Days
6	100-125	10^5 - 10^6	10^4 - 10^5	5×10^3 - 10^4	Weeks
7	75-100	10^6 - 10^7	10^5 - 10^6	10^4 - 5×10^4	Months
8	50-75	10^7 - 10^8	10^6 - 5×10^6	5×10^4 - 10^5	Years
9	25-50	10^8 - 10^9	5×10^6 - 10^7	10^5 - 10^6	Decades
10	0-25	> 10^9	> 10^7	>10^6	> Decades

As discussed in section 4.1.1 the potential for the dispersion of a chemical in the atmosphere can be estimated using its molecular weight. The heavier a chemical is the less likely it is that it will remain in the air and disperse. Most of the gases which will disperse readily in the atmosphere such as light organics with one to four carbon atoms per molecule (C1-C4) and inorganic gases such as carbon dioxide and nitrogen have molecular weights less than 100g/mole while heavier chemicals which can still

volatilise and disperse such as aromatics can have molecular weights several times greater than this. Thus the scoring system in Table 4.10 incorporates a range of molecular weights from 0 up to 225 in order to represent a large range of chemicals which will exhibit different dispersion behaviour in the atmosphere.

The potential mobility of a chemical in an aquatic system is partly determined by its solubility. The solubility of chemicals can vary immensely including chemicals which are virtually insoluble such as cadmium sulphide (10 ppb @ 15°C) and others that are almost completely miscible such as n-butanol (S = 10^8 ppb @ 15°C). The scoring system for solubility which is shown in Table 4.10 was designed in order to cover the full range of these values.

Lyman et al (1982) indicated that the typical values for the soil adsorption constant K_{oc} were between the values of 1.0 and 1.0×10^7 (µg/go.c.)/(µg/ml). The units for these values are mass of chemical adsorbed per mass of organic carbon in the soil, per mass of chemical per volume of liquid. These values were chosen to set the ranges for the scoring system presented in Table 4.10 with the limits defined by chemicals such as 1,1,1-trichloroethane (K_{oc} = 0.5) and the pesticide Mirex (K_{oc} = 2.4×10^6).

The units of both the numerator and denominator of the BCF as defined in equation (4.3) must be the same in order to make it dimensionless. Typical values of the dimensionless BCF are in the range from approximately 1 for chemicals which exhibit minimal bioconcentration such as acetone with a BCF of 0.69 (Howard et al, 1990) to over 100,000 for chemicals such as Aroclor 1254 (2,2',4,5,5'-pentachlorobiphenyl) which readily bioconcentrate (Lyman et al, 1982). These two extreme limits were chosen for the BCF scoring system shown in Table 4.10.

The half-life of a chemical can be used as a measure of the rate at which it degrades in the environment and it is predominantly used in EniVal to determine whether or not the chemical will degrade before exhibiting long-term effects. As discussed previously in Chapter 3 long-term effects are those considered over a period of years

while short-term effects are limited to hours and days. LaGrega et al (1994) identified the four different classifications of exposure presented in Table 4.11.

Table 4.11 Exposure periods

Exposure type	Duration
Acute	1 day
Sub-acute	10 days
Sub-chronic	2 weeks - 7 years
Chronic	7 years - lifetime

These four classifications were extended to include the full range of possible half-lives of chemicals given in Table 4.10.

The dispersion of a pollutant is very dependent on local environmental conditions and the scoring systems for the location factors are designed to provide measures of the extent to which these effects will contribute to the distribution of a chemical in a given medium. The factors vary for the atmospheric and the water systems as presented below.

The atmospheric location factors comprise of two components, the first of which represents the typical atmospheric stability conditions at the site of the discharge. These conditions will vary considerably over time and so it may not be possible to obtain a representative set of conditions. As a result, the worst case scenario should be studied to determine the behaviour of the chemical under the most extreme set of conditions possible. The stability of the atmosphere is a strong function of the surface wind speed which can be measured easily. Table 4.12 shows how the stability score (STAB) is related to the surface wind speed. The second component representing the local conditions is the topographical parameter (TOPO) which provides a measure of the local topography of the region as illustrated in Table 4.13. The two parameters defined above are multiplied together to provide an overall atmospheric location factor.

Table 4.12 Atmospheric stability factor

Wind speed at a height of 10 m (m/s)	STAB
< 2	1
2 - 3	2
3 - 5	3
5 - 6	4
> 6	5

Table 4.13 Local topography score

Local site features	TOPO
Top of a hill	1
Flat surroundings	1.5
Valley	2

The dispersion of a pollutant in a water system is dependent on two main features of the local system, namely:

1. the size of the water body; and
2. the rate at which it is flowing.

Scores are assigned to these two factors and then multiplied together to provide an overall location factor score. Examples of some typical values are shown in Table 4.14.

Table 4.14 Water system location factors

Flow	Score	Size	Score	Total
High	1	Large	3	3
High	1	Small	5	5
Low	2	Large	3	6
Low	2	Small	5	10

4.4 Summary

The quantification of the impact of a chemical on the whole environment is a very complicated and subjective process. This chapter has presented all of the parameters which are utilised by EniVal to provide a measure of the overall environmental impact. Each of these parameters is linked to an individual scoring system whereby the raw data values are converted to effect scores ranging in value between either 0 and 10 or 1 and 10. The impact scores provide a consistent measure of the particular environmental effects of a pollutant throughout the atmosphere, water and soil covering issues related to the damage and modification of the environment as well as the persistence of a pollutant in a given environment. The combination of these scores to provide an overall measure of environmental impact is presented in Chapter 5.

Chapter 5

The calculation of impact scores

The scores derived from the raw data for the parameters are combined from the lowest level of EniVal up through the tree structure to the apex value for the total impact. As discussed in the following sections, the scores are combined using weighted sums and multiplication where appropriate.

There is a range of tools and methods which have been developed to combine environmental impact parameters using weighted sums. The weightings for these sums have been chosen using a wide variety of techniques ranging from those of Hope et al (1992) which were based on public opinion to those incorporated in the Eco-indicator (Goedkoop, 1995) based on the distance-to-target principle. In many cases the weightings have been derived based on the opinions of the developers of the impact tools combined with expert knowledge of the field, such as in the risk indices developed by Teague, Mapp and Bernardo (1995) and the water quality index of Brown et al (1970). Most of the weightings incorporated in EniVal are based on knowledge of the interactions between pollutants and the environment.

Each of the short-term and long-term branches is divided into the three further sub-branches of damage, modification and persistence. The following sections examine each of these sub-branches in detail to describe the techniques used to incorporate each of the parameters. Section 5.3 provides a worked example of the combination of all of the scores for the sample pollutant, benzene.

5.1 Short-term impact scores

As outlined in Chapter 4 the branches which quantify the short-term impact scores for each of the environmental media utilise different parameters. These parameters are distributed between the damage, modification and persistence branches of the tree. Each of these branches is examined in detail in the following sections.

5.1.1 Damage

The damage branch for the assessment of the short-term impact of a pollutant incorporates the same combination techniques for each of the environmental media.

Toxicity is assessed using only the relevant acute toxicity parameter (the OEL for the atmospheric system and the EC_{50} for the water and soil systems) as discussed in Chapter 4. The acute toxicity score is then combined with the total score for hazards.

The total score for hazards is quantified using an equally weighted combination of the flammability and explosivity scores as shown in equation (5.1). In comparison, the Dow Fire and Explosion Index (FEI) (Dow, 1987) has a factor ranging from 0.15 to 3.0 for the flammability of materials involved in the process. Another factor measures the potential for explosion and its values range between 0.25 and 2.0. In this case the maximum weightings for flammability and explosivity are 60% and 40% respectively. However the FEI only incorporates dust explosions, while EniVal incorporates both detonation and explosive decomposition. Thus for EniVal, an equal weighting of 50% was applied to each score.

$$HAZ = 0.5 \times FLAM + 0.5 \times EXPL \qquad \textbf{(5.1)}$$

where:

HAZ	is the score for hazards;
FLAM	is the score for flammability; and
EXPL	is the score for explosivity.

The overall short-term damage score which combines the toxicity and hazards scores is calculated using the formula shown in equation (5.2).

$$DAM_{ST} = 0.8 \times TOX_{ST} + 0.2 \times HAZ \qquad \textbf{(5.2)}$$

where:

DAM_{ST}	is the score for short-term damage; and
TOX_{ST}	is the score for acute toxicity.

The toxicity score is assigned a much heavier weighting than the hazards score due to the greater risks associated with toxic effects. Explosions or fires are generally single incidents which will not usually occur unless conditions vary from the normal. However, the mere presence of a toxic pollutant in the environment provides the possibility of immediate and perhaps permanent damage to humans and their

surrounding environment, hence the greater weighting factor. The FEI incorporates a toxic material factor of between 0.2 and 0.8 which is much less than the maximum possible sum of the factors for flammability and explosivity (5.0) as discussed above. However the FEI is predominantly used to measure the potential for a fire or explosion as a risk assessment tool and not the likelihood of toxic effects. EniVal was designed to analyse the total impact of pollutants on the environment rather than the inherent safety of the process. Thus a much greater weighting is applied to the hazards which can result in serious, widespread harm to the environment.

5.1.2 Modification

Each of the three modification branches for the short-term impact of a pollutant on the environment incorporates a score for the degradation of the aesthetics of the local environment. These scores consider visual as well as olfactory problems as discussed in Chapter 4. As each modification branch only incorporates one aesthetics parameter there are no combination techniques required.

5.1.3 Persistence

Due to the slow dispersion processes in the soil system the quantification of the short-term impact of a pollutant in the soil system does not include an assessment of the persistence of that pollutant as described in Chapter 4. However, both the atmospheric and water systems incorporate a persistence branch for assessing the dispersion and degradation of the pollutant in the environment. The dispersion of the pollutant in the atmosphere and the water is assessed using the techniques outlined in equations (5.3) and (5.4) respectively. The scores for the mobility parameters (molecular weight and solubility) are added to the location factors using equal weightings. Very few impact analysis tools incorporate measures of the environmental fate of pollutants. For the development of EniVal it was assumed that the physical property of the pollutant related to dispersion and the local factors affecting dispersion were of equal importance to the overall dispersion scores. Thus EniVal incorporates equal weightings for the scores for the dispersion parameters.

$$DISP_{ST,A} = 0.5 \times MWSc + 0.5 \times LOC_A \qquad (5.3)$$

where:

$DISP_{ST,A}$ is the score for the short-term atmospheric dispersion;

MWSc is the score for the molecular weight; and

LOC_A is the score for the atmospheric location factors.

$$DISP_{ST,W} = 0.5 \times SOL + 0.5 \times LOC_W \quad (5.4)$$

where

$DISP_{ST,W}$ is the score for the short-term water dispersion;

SOL is the score for the solubility; and

LOC_W is the score for the water location factors.

The degradation parameter for the short-term utilises the half-life of a pollutant to determine whether or not it will persist long enough for it to exhibit its potential harmful effects on the environment. The parameter is scored as either 0 or 1 and is incorporated as a weighting for the dispersion parameters as shown in equation (5.5).

$$PERS_{ST,M} = DISP_{ST,M} \times DEG_{ST,M} \quad (5.5)$$

where:

$PERS_{ST,M}$ is the score for the short-term persistence for medium M;

$DISP_{ST,M}$ is the score for the short-term dispersion for medium M;

$DEG_{ST,M}$ is the score for the short-term degradation for medium M; and

M is the subscript for the atmosphere and the water systems.

5.1.4 Overall short-term impact

The overall short-term impact in the atmospheric and water systems is assessed by a combination of the damage, modification and persistence scores calculated using equations (5.1) to (5.5). The damage and modification branches provide measures of the possible harmful effects of a given pollutant, while the persistence branch quantifies the likely extent of these effects. Thus the combination of these three branches incorporates similar techniques to those used for quantifying risk whereby the hazard associated with a given risk is multiplied by the probability of its occurring. The formula which combines these damage, modification and persistence scores (each of which ranges from 0 to 10) for the atmospheric and water systems is shown in equation (5.6).

$$I_{ST,M} = (0.7 \times DAM_{ST,M} + 0.3 \times MOD_{ST,M}) \times 0.1 \times PERS_{ST,M} \quad (5.6)$$

where

$I_{ST,M}$	is the score for the short-term impact for medium M;
$DAM_{ST,M}$	is the score for the short-term damage in medium M;
$MOD_{ST,M}$	is the score for the short-term modification in medium M;
$PERS_{ST,M}$	is the score for the short-term persistence in medium M; and
M	is the subscript for the atmosphere and the water systems.

As previously discussed, a persistence branch is not included for the soil system and the combination of the two soil effects branches is shown in equation (5.7).

$$I_{ST,S} = 0.7 \times DAM_{ST,S} + 0.3 \times MOD_{ST,S} \quad (5.7)$$

where:

$I_{ST,S}$	is the score for the short-term soil impact;
$DAM_{ST,S}$	is the score for the short-term damage in the soil; and
$MOD_{ST,S}$	is the score for the short-term modification in the soil.

For all three environmental media the damage scores are weighted more heavily than the modification scores due to the seriousness of the associated effects. The toxic and hazardous characteristics of a chemical represent direct impacts on the target whereas the aesthetic impacts measured in the modification branch do not directly threaten the health of humans or other living creatures in the environment. In the Rhône-Poulenc (HMIP, 1992a) performance indices different weighting factors are applied to different parameters. Red-list substances such as mercury receive factors of 1,000 while other parameters are assigned much smaller weightings e.g. suspended solids in the aqueous environment (0.3). As with those incorporated in EniVal, the Rhône-Poulenc weightings also recognise the relative importance of the different effects that pollutants can have on the environment. The persistence scores for the atmospheric and water systems are given weightings of 0.1 to ensure that the final impact scores remain on a scale from 0 to 10.

The impact score for each medium is then multiplied by its respective short-term fractional distribution ($F_{ST,M}$) as determined by the medium to which the pollutant is discharged. In the calculation of EniVal it is assumed that in the short-term only the acute effects which occur in the medium to which the pollutant is released need to be considered. The weighted impacts are then summed to provide an overall short-term impact for the given pollutant as shown in equation (5.8).

$$I_{ST} = F_{ST,A} \times I_{ST,A} + F_{ST,W} \times I_{ST,W} + F_{ST,S} \times I_{ST,S} \quad (5.8)$$

where:

I_{ST} is the score for the total short-term impact; and

$F_{ST,M}$ is the short-term fractional distribution for the medium M (atmosphere, water and soil).

5.2 Long-term

The following section examines the combination of the parameters used to quantify the long-term impact of a given pollutant. It also describes the techniques used to combine both the short-term and the long-term data to provide an overall impact. Section 5.3 studies this combination further for the sample chemical benzene.

5.2.1 Damage

The damage branch for the assessment of the long-term impact of pollutants on the environment is almost identical to that utilised for the short-term assessment, the only difference being the inclusion of an extra parameter to represent the chronic toxicity of pollutants. The chronic toxicity parameter is combined with the acute toxicity parameter in the lowest level of EniVal using the formula which is shown in equation (5.9). The risk indices developed by Teague et al (1995) incorporate equal weightings for chronic and acute toxicity parameters. However in EniVal, the weighting assigned to the chronic toxicity score is greater than that for the acute toxicity score as immediate acute effects have already been considered in the short-term assessment. Also the chronic effects, by their very nature tend to result in the prolonged, continual degradation of health which is of greater concern in the long-term.

$$TOX_{LT} = 0.4 \times TOX_{ST} + 0.6 \times TOX_{CHRON} \quad (5.9)$$

where:

TOX_{LT} is the score for the long-term toxicity; and

TOX_{CHRON} is the score for the chronic toxicity.

The toxicity parameter determined using equation (5.9) is combined with the hazards parameter defined in equation (5.1) using the formula in equation (5.10). As discussed in section 5.1.1 the toxicity scores are weighted more heavily than those for the hazards to account for the greater potential damage to the overall environment.

$$DAM_{LT} = 0.8 \times TOX_{LT} + 0.2 \times HAZ \quad (5.10)$$

where:

DAM_{LT} is the score for the long-term damage.

5.2.2 Modification

The modification branches for the long-term assessment incorporate different parameters to those for the short-term analysis. The parameters which are included in the long-term modification branches vary for each environmental medium according to the relevant effects as discussed in Chapter 4.

In the atmospheric system, the three major environmental concerns which are included are acid rain, ozone production and global warming. Each of these effects is considered equally important, hence they are combined with equal weightings as shown in equation (5.11). A Life-Cycle Assessment (LCA) approach for assessing pollution prevention opportunities developed by Curran (1995) incorporates 25 parameters, several of which including the photochemical oxidant creation potential and the global warming potential are similar to those incorporated in EniVal. As in EniVal, the LCA-based approach incorporates equal weightings for these parameters. However the distance-to-target method for determining parameter weightings as used in the determination of the Eco-indicator (Goedkoop, 1995) assigns very different

weightings to the scores for the greenhouse effect, acidification and ozone depletion (2.5, 10 and 100 respectively). These weightings are based on the current extent of the problems compared to some desirable level rather than the actual impacts on the environment. Thus the distance-to-target assessment is more political than scientific and the equal weightings utilised by the LCA-based approach are more appropriate for the impact-based EniVal.

$$MOD_{LT,A} = 0.333 \times ACID + 0.333 \times OC + 0.333 \times GW \quad (5.11)$$

where:

$MOD_{LT,A}$	is the score for the long-term atmospheric modification;
ACID	is the score for the acid rain formation potential;
OC	is the score for the ozone creation potential; and
GW	is the score for the global warming potential.

The water and soil systems incorporate only one parameter each, namely oxygen depletion and land reuse respectively as described in Chapter 4. These parameters provide the total modification scores for the water and soil systems as shown in equations (5.12) and (5.13).

$$MOD_{LT,W} = DEOX \quad (5.12)$$

where:

$MOD_{LT,W}$	is the score for the long-term water modification; and
DEOX	is the score for the oxygen depletion potential.

$$MOD_{LT,S} = LAND \quad (5.13)$$

where:

$MOD_{LT,S}$	is the score for the long-term soil modification; and
LAND	is the score for limitations to land reuse.

5.2.3 Persistence

In the atmospheric system EniVal assesses the long-term persistence of a chemical using a dispersion parameter (molecular weight) and a degradation parameter (half-

life) as discussed in Chapter 4. These two parameters are combined as shown in equation (5.14).

$$PERS_{LT,A} = 0.2 \times MWSc + 0.8 \times DEG_{LT,A} \quad \textbf{(5.14)}$$

where:

$PERS_{LT,A}$	is the score for the long-term atmospheric persistence; and
$DEG_{LT,A}$	is the score for the long-term atmospheric degradation.

The long-term analysis differs from the short-term assessment in that the dispersion parameter and the degradation parameter are summed rather than multiplied. The short-term assessment utilises the degradation parameter to determine whether or not the pollutant will be present in the environment long enough to cause the acute effects. However in the long-term, the dispersion processes become less important and the extent to which the chemical will persist in the atmosphere is predominantly determined by how long it takes to degrade. Thus the degradation parameter is now added to the dispersion parameter and assigned a weighting of 80% compared to only 20% for the dispersion parameter.

The water and soil persistence branches incorporate an extra parameter which provides a measure of the potential for a pollutant to bioconcentrate. The persistence branches are calculated using the formula shown in equation (5.15).

$$PERS_{LT,M} = 0.15 \times DISP_{LT,M} + 0.55 \times DEG_{LT,M} + 0.3 \times BC \quad \textbf{(5.15)}$$

where:

$PERS_{LT,M}$	is the score for the long-term persistence in medium M;
$DISP_{LT,M}$	is the score for the long-term dispersion in medium M;
$DEG_{LT,M}$	is the score for the long-term degradation in medium M;
BC	is the score for the bioconcentration factor; and
M	is the subscript for either the water or the soil system.

For the water system the dispersion parameter is the solubility score, the degradation parameter is the water half-life score and the bioconcentration parameter is the

bioconcentration factor score. The soil system uses the same parameter for bioconcentration but incorporates the soil adsorption constant rather than the solubility for dispersion and the terrestrial half-life for degradation. As for the atmospheric system the degradation parameter is considered more important than the dispersion.

5.2.4 Overall Impact

A similar formula to that used for the short-term assessment to combine the damage, modification and persistence scores is used to provide an overall long-term impact score for each medium as shown in equation (5.16).

$$I_{LT,M} = (0.7 \times DAM_{LT,M} + 0.3 \times MOD_{LT,M}) \times 0.1 \times PERS_{LT,M} \quad (5.16)$$

where:

$I_{LT,M}$	is the score for the long-term impact in medium M;
$DAM_{LT,M}$	is the score for the short-term damage in medium M;
$MOD_{LT,M}$	is the score for the long-term modification in medium M;
$PERS_{LT,M}$	is the score for the long-term persistence in medium M; and
M	is the subscript for the either the atmosphere, the water or the soil system.

The three long-term impact scores (atmospheric, water and soil) are then combined using the long-term fractional distributions for each medium as calculated by the fate and distribution models discussed in Chapter 3 to determine the overall long-term impact for a given pollutant. The formula for the combination of the three medium-specific impacts is shown in equation (5.17).

$$I_{LT} = F_{LT,A} \times I_{LT,A} + F_{LT,W} \times I_{LT,W} + F_{LT,S} \times I_{LT,S} \quad (5.17)$$

where:

I_{LT}	is the score for the total long-term impact; and
$F_{LT,M}$	is the long-term fractional distribution for medium M (atmosphere, water or soil).

The overall short-term impact and the overall long-term impact are then combined with equal weightings as shown in equation (5.18). There are few techniques which separate the short-term and long-term effects of pollutants and so the parameters are often all combined together in the one analysis. However, the final combination shown in equation (5.18) is similar to that used in the risk indices of Teague et al (1995) where acute and chronic toxic effects are weighted equally.

$$I = 0.5 \times I_{ST} + 0.5 \times I_{LT} \qquad (5.18)$$

where:

I is the score for the overall, total impact.

5.3 Worked example

The first step in analysing a new pollutant is to collect all of the data which is required to fully describe the environmental impact of the chemical as discussed in Chapter 4. Table 5.1 shows the raw data for each of the parameters for the sample chemical (benzene) along with the relevant data sources and the scores which have been assigned to the parameters using the scoring systems described in Chapter 4.

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Table 5.1 Raw data and parameter scores for benzene

Parameter	Value	Source	Score
OEL	16 ppb	(HSE, 1994)	4
EC_{50}	75 ppm	(Kaiser and Palabrica, 1991)	1
Reproductivity test	Not available	-	-
Carcinogenicity	Class A	(La Grega et al, 1994)	10
Toxic metabolites	-	*[†]	2
log(Kow)	2.13	(Howard, 1990)	0.7
Pollutant type	0	*	0
Material factor	16	(Dow, 1987)	3
Explosive decomposition		*	0
Detonation		*	0
Solubility	1.8×10^{6} ppb	(Howard, 1990)	8
Vapour Pressure	12.7 kPa	(Howard, 1990)	2
BCF	4	(Howard, 1990)	2
Half-life A	2.1 days	(Howard et al., 1991)	6
Half-life W	5 days	(Howard et al., 1991)	6
Half-life S	5 days	(Howard et al., 1991)	6
Acid rain		*	5
GWP	0	(HMIP, 1994b)	0
POCP	19	(HMIP, 1994b)	2
UOD	16.02	*	6
Aesthetics A	0	*	0
Aesthetics W	0	*	0
Aesthetics S	0	*	0
Molecular weight	78.11 g/gmole	(Howard, 1990)	7
Henry's Law constant	5.43×10^{-3} atm m^3 / gmole	(Howard, 1990)	
Koc	98 mg/g o.c. / mg/l	(Howard, 1990)	3
Land reuse	0	(ICRCL, 1987)	5

5.3.1 Combinations

Using the scores provided in Table 5.1 a total impact score can be calculated for benzene. The assessment of the short-term damage tree is different for the atmospheric system and the soil and water systems as discussed in section 5.1.1. Equations (5.1) and (5.2) are utilised to determine the short-term damage branches

[†] Data source * means that the value was calculated from an appropriate formula or was estimated using either the user's or expert opinion.

for the three environmental sub-systems. The results from these equations for the benzene data are shown in Table 5.2.

Table 5.2 Short-term damage scores

System	Toxicity parameter	Acute toxicity	Hazards	Short-term damage
Atmosphere	OEL	4	1.5	3.5
Water	EC_{50}	1	1.5	1.1
Soil	EC_{50}	1	1.5	1.1

The short-term modification parameters only consider the aesthetic impacts of the pollutant and as benzene is a colourless liquid with a pleasant odour (Material Safety Data sheets, MSDS) the aesthetics scores for all three media have the value of 0 as shown in Table 5.3.

Table 5.3 Short-term modification scores

System	Aesthetics score	Short-term modification
Atmosphere	0	0
Water	0	0
Soil	0	0

As discussed in Chapter 4 there is no short-term persistence branch for the soil system. The short-term persistence of benzene in the atmospheric and water systems is described using the formulae in equations (5.3) to (5.5) to yield the persistence scores shown in Table 5.4.

Table 5.4 Short-term persistence scores

System	Location factors	Mol. Wt. or Solubility	Dispersion	Degradation	Short-term persistence
Atmosphere	5	7	6	1	6
Water	5	8	6.5	1	6.5

Table 5.5 shows the overall short-term impact of benzene obtained through the combination of the short-term damage, modification and persistence scores presented in Tables 5.2 to 5.4.

Table 5.5 Short-term impact scores for benzene

System	Damage	Modification	Persistence	Short-term impact
Atmosphere	3.5	0	6	1.5
Water	1.1	0	6.5	0.5
Soil	1.1	0		0.8

5.3.2 Long-term Impact

The long-term damage branches for benzene incorporate the same parameters as for the short-term assessment but also include a score for the chronic toxicity of benzene. As discussed in Chapter 4 the chronic toxicity is assessed using a combination of three different parameters:

- log(Kow);
- potential for forming toxic metabolites; and
- reproductivity effects or carcinogenicity depending on data availability.

No data was available for the reproductivity tests for benzene so carcinogenicity data was utilised instead. The final overall chronic toxicity score is shown in Table 5.6 along with the values for each of the three parameters defined above.

Table 5.6 Chronic toxicity score

Carcinogenicity class	Carcinogenicity score	Metabolites score	log(Kow) score	Chronic toxicity score
A	10	2	0.7	4.2

The chronic toxicity score for benzene in Table 5.6 is combined with the acute toxicity and the hazards scores using equation (5.9) to give the results in Table 5.7.

Table 5.7 Long-term damage scores

System	Acute toxicity parameter	Acute toxicity	Chronic toxicity	Hazards	Long-term damage
Atmosphere	OEL	4	4.2	1.5	3.6
Water	EC_{50}	1	4.2	1.5	2.6
Soil	EC_{50}	1	4.2	1.5	2.6

Each of the three environmental media incorporates different parameters to assess the long-term modification branches.

Table 5.8 Long-term modification scores

System	Acid rain	POCP	GWP	UOD	Land reuse	Long-term modification
Atmosphere		0	2			1
Water	5			6		6
Soil					5	5

The assessment of the long-term persistence branches are different for the atmospheric and the water and soil systems in that the analysis of the atmospheric system only incorporates dispersion and degradation parameters while the water and soil systems include a bioconcentration score as well. The combinations of all of these parameters to provide the overall persistence scores are shown in Table 5.9.

Table 5.9 Long-term persistence scores

System	Dispersion	Degradation	Bioconcentration	Long-term persistence
Atmosphere	7	6		6.2
Water	8	6	2	5.1
Soil	3	6	2	4.4

Table 5.10 shows the overall long-term impact of benzene obtained through the combination of the long-term damage, modification and persistence scores presented in Tables 5.6 to 5.9.

Table 5.10 Long-term impact scores for benzene

System	Damage	Modification	Persistence	Long-term impact
Atmosphere	3.6	1	6.2	1.7
Water	2.6	6	5.1	1.8
Soil	2.6	5	4.4	1.5

5.3.3 Overall Impact

To obtain the overall impact of benzene on the whole environment, the short-term impacts from Table 5.5 and the long-term impacts in Table 5.10 must be combined using the short-term and long-term fractional distributions respectively. For the purposes of this example it is assumed that the benzene is discharged to the atmosphere hence the values of the short-term fractional distribution (F) shown in Table 5.11.

Table 5.11 Short-term fractional distributions

System	F_{ST}
Atmosphere	1
Water	0
Soil	0

The long-term fractional distributions shown in Table 5.12 are estimated using the model developed for organic chemicals in Chapter 3 which incorporates the Henry's Law constant and the soil adsorption constant data provided in Table 5.1.

Table 5.12 Long-term fractional distributions

System	F_{LT}
Atmosphere	0.68
Water	0.16
Soil	0.16

All the fractional distribution and impact scores derived in Tables 5.2 to 5.12 are combined to provide a total impact on the environment for an atmospheric discharge of benzene as shown in Table 5.13.

Table 5.13 Overall impact scores for benzene

System	Short-term impact	F_{ST}	Long-term impact	F_{LT}	Impact	Total Impact
Atmosphere	1.5	1	1.7	0.68	1.33	1.6
Water	0.5	0	1.8	0.16	0.14	
Soil	0.8	0	1.5	0.16	0.12	

5.4 Chemicals

A summary of the impact scores for thirty-two different chemicals is presented in Table 5.14. The chemicals which are listed were taken from the emission summaries for the industrial processes that were used to design and test EniVal as described in detail in Chapter 6. The physical and chemical data used to calculate the impact scores for each of these chemicals is presented in Appendix E. The impacts for the thirty-two chemicals were determined assuming that each pollutant would be discharged to the environmental medium indicated in the second column of Table 5.14. These media were selected to represent the most common types of discharge of

the given chemicals. As shown in Table 5.14 the impact scores range from 0.2 to 4.8 on a scale from 0 to 10. While the maximum score of 4.8 may not appear to be high on a scale out of 10, there are very few pollutants which will have an impact score of greater than 5. The maximum score of 10 can only be obtained when every single parameter on the bottom level of the tree is at its maximum value (10), which is unlikely to occur. Thus pollutants with impact scores around 5 are considered to have a very high potential environmental impact.

Table 5.14 Summary of pollutant impacts

Chemical	Medium	Impact (max. 10)
Water	A	0.2
Calcium sulphate	S	0.4
Methanol	W	0.7
Sodium nitrate	S	0.8
CO_2	A	0.9
Sulphuric acid	A	0.9
Ethane	A	0.9
Ethyl chloride	A	1.0
Particulates	A	1.1
Hydrogen	A	1.1
Pentane	A	1.1
Aluminium chloride	S	1.4
Paraxylene	A	1.4
Ethylene	A	1.5
Hydrogen chloride	A	1.6
Toluene	A	1.6
Benzene	A	1.6
Chlorine	A	1.7
Sodium Hydroxide	W	1.7
Formaldehyde	A	1.8
Nitrobenzene	A	2.0
Nitric acid	A	2.0
SO_2	A	2.0
NO_x	A	2.2
Iron sulphate	S	2.3
Zinc	S	3.1
Copper	S	3.3
Mercury	S	4.0
Cadmium	S	4.7
Lead	S	4.7
Nickel	S	4.8
Chromium	S	4.8

The minimum impact score occurs for an atmospheric discharge of water, or steam. The impact is so low because the only score greater than zero in the analysis is the atmospheric aesthetics score due to the visual nature of the steam plume. As may be

expected the chemicals with the greatest impact scores are the heavy metals, the majority of which have impacts of greater than 4. As discussed at the beginning of section 5.4 these scores are at the upper end of the possible range of impact scores. Other chemicals with relatively high impacts include aromatics such as benzene and toluene and other commonly identified pollutants such as NO_x and SO_2.

The impact scores presented in Table 5.14 are meaningless on their own in assessing the environmental impact of a chemical process. They must be combined with discharge data in order to provide a full description of the impacts caused by the emission of the pollutants.

5.5 Summary

EniVal determines the total impact of a chemical using a combination of twenty-eight different parameters. These parameters are combined using a tree structure and both weighted sums and multiplicative techniques to provide a single value for the overall impact. This chapter has examined all of the techniques used to combine the parameters and has provided a sample calculation for benzene to show how the raw data for a given pollutant can be transformed to provide a single impact value. Chapter 6 provides a brief summary of the 12 industrial processes used to further develop EniVal. In Chapter 7 the discharge data from these 12 processes are combined with the impact data derived using the techniques described in Chapters 4 and 5 to determine the overall impact of a given chemical process.

Chapter 6

Industrial processes

This chapter presents the 12 industrial processes which have been used to further develop and test EniVal. How the data from these processes has been used to develop the combination techniques for the impact data and the discharge data is presented in detail in Chapter 7. The 12 processes are:

1. ethyl chloride production;
2. nitrobenzene production;
3. Formox process;
4. paraxylene production;
5. hydrogen chloride production;
6. specialty chemicals production;
7. four industrial boiler plants; and
8. two cement clinker plants.

To ensure that the combination of the effect parameters defined in Chapter 4 provides the most accurate measures possible of environmental impact, real emission data from these processes have been incorporated into the analyses. Most of the emission data were taken both from the applications made to HMIP by companies for IPC registration of their operations, and from the authorisations which were granted for these applications. The data for the cement clinker plants was taken from a case study presented in the ENDS report (1995).

The processes were selected to represent a range of different chemical operations and to incorporate emissions to all three media (atmosphere, water and soil). The following sections contain brief descriptions of each of the processes along with simple schematic diagrams showing the major unit operations involved. A summary of the quantities and types of emissions for each of the processes is also presented. Within this summary the impacts scores for the all of the pollutants discharged from the relevant process are also provided. Table 6.1 defines the nomenclature that is used in these summaries to describe the emission quantities and the media to which

they are discharged. This nomenclature can also be found at the beginning of the thesis in the general list on page xi.

Table 6.1 Nomenclature for emission summaries

Nomenclature	
A	atmosphere
W	water
L	land
OSD	off-site disposal
ETP	on-site effluent treatment plant
tpd	tonnes per day
tpa	tonnes per annum
tp5a	tonnes per five years
kgpa	kilograms per annum

6.1 Ethyl chloride production

Ethyl chloride is used in the manufacture of motor fuel lead antiknock compounds. This ethyl chloride plant, constructed in 1971, has a maximum operating capacity of 55,000 tonnes per annum although it typically operates at 45,000 tonnes per annum based on 1990/1991 figures. Currently the plant operates for 310 days each year with a 97% conversion of ethylene to ethyl chloride (HMIP, 1993a).

In this process ethyl chloride is formed via a two stage reaction. The first step is the combustion of chlorine in hydrogen to produce hydrogen chloride gas (HCl).

$$H_2 + Cl_2 \xrightarrow[1\ atm]{> 2000\ °C} 2HCl$$

HCl gas is then reacted with ethylene in the liquid phase using crude ethyl chloride as the solvent and dissolved aluminium chloride for the catalyst.

$$HCl + C_2H_4 \xrightarrow[3\ barg]{50\ °C} C_2H_5Cl \qquad (C_2H_4 \text{ conversion} = 97\%)$$

Three side reactions need to be strictly controlled to avoid the production of two significant by-products i.e. polymers and dichloroethane.

$$n(C_2H_4) \rightarrow (C_2H_4)_n$$ polymerisation (C_2H_4 conversion = 3%) where n = 1,500 - 1,800

$$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2$$

$$C_2H_5Cl + HCl \rightarrow C_2H_4Cl_2 + H_2$$

] Dichloroethane (Trace)

A simplified flowsheet for this process is given in Figure 6.1. Hydrogen is imported to the plant, compressed and then dried in a molecular sieve adsorber. Liquid chlorine is fed to an evaporator to produce chlorine gas at the same pressure as the hydrogen. These two gases (hydrogen and chlorine) are fed to burners where the hydrogen chloride is formed. The burners are operated with a slight excess of hydrogen to ensure complete reaction of the chlorine. Hydrogen chloride is then cooled, dried using sulphuric acid, filtered and compressed before being fed to the reaction vessel which operates at the boiling point of ethyl chloride.

High pressure ethylene gas is fed into the base of the reactor along with the hydrogen chloride. The heat of reaction causes the ethyl chloride to boil off and the product is then collected and condensed.

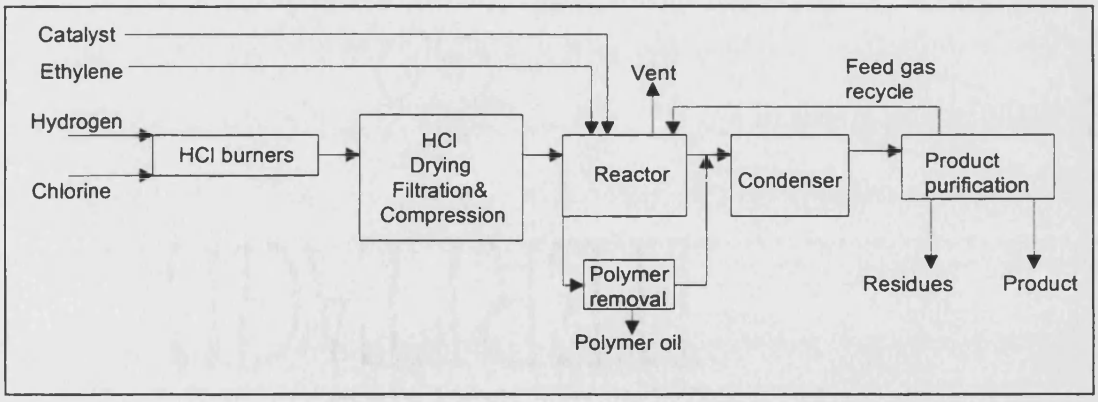

Figure 6.1 Ethyl chloride production schematic diagram

Unreacted feed gases are compressed and recycled to the reactor. A vent is used to remove the inerts (mainly excess hydrogen) from the condenser to prevent the it from being blanketed. The ethyl chloride product is purified in two distillation columns operated in series. The first column removes the lights (mainly hydrogen chloride) and the second removes the ethyl chloride product and leaves a heavy bottom waste stream of ethyl chloride residues. Polymer and deactivated catalyst are continually

removed from the reactor by flashing a flow of reactor solution. The ethyl chloride is returned to the main reactor condenser and the catalyst is removed as a separate organic phase which is discharged to the effluent treatment plant. Table 6.2 shows the emissions which have been reported for this process.

Table 6.2 Ethyl chloride production emission summary

Substance	Release	Units	Medium	Impact
Ethyl chloride	418	tpa	A	1.4
Ethylene	0.2	tpa	A	1.7
Ethane	4×10^{-3}	tpa	A	1.3
Hydrogen chloride	3×10^{-4}	tpa	A	1.3
Ethyl chloride residues	647	tpa	OSD (Incineration)	1.4
Hydrogen chloride	1,070	tpa	W (ETP)	1.3
VOC	11	tpa	W (ETP)	1.8
Aluminium chloride	49	tpa	W (ETP)	1.4
Mercury	1×10^{-6}	tpa	W (ETP)	4.2

6.2 Nitrobenzene production

This nitrobenzene process has a maximum operating capacity in excess of 300,000 tonnes per annum (HMIP, 1994c) and operates typically for 312.5 days per annum.

Sulphuric acid (>95 wt%) and nitric acid (approximately 70 wt%) are mixed and contacted with benzene to produce the nitrobenzene product. Conversions in excess of 99% are achieved.

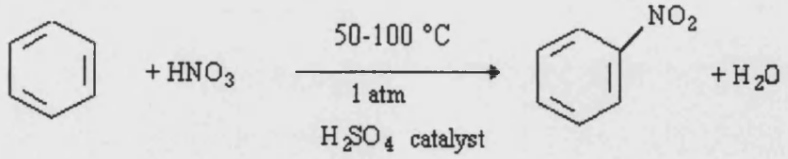

Figure 6.2 shows a simplified schematic diagram of the major unit operations. The recovered sulphuric acid catalyst, diluted by the water produced in the reaction, is reconcentrated by direct contact with hot air before being returned to the start of the process. The nitrobenzene product is extracted with water and dilute alkali prior to a steam distillation stage. This stage removes any unreacted benzene which is recycled within the process.

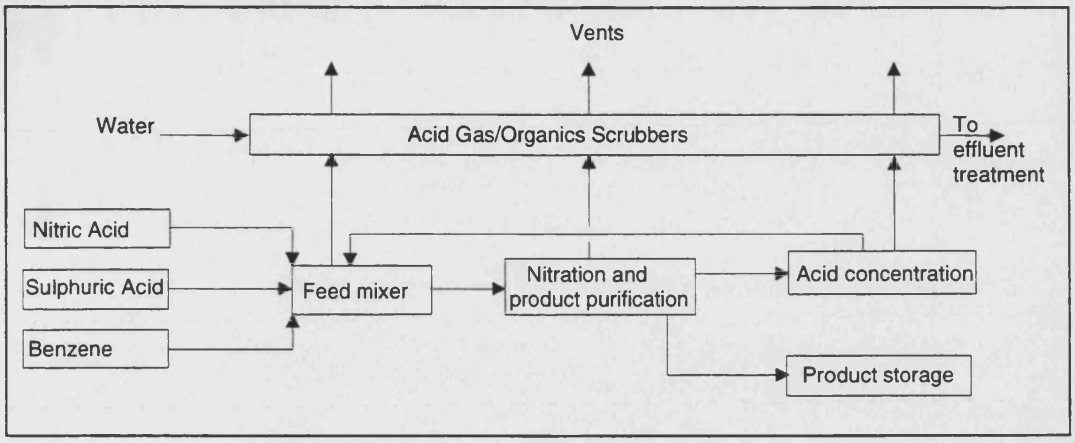

Figure 6.2 Nitrobenzene production schematic diagram

Chapter 9 examines the nitrobenzene production process in greater detail using case studies to analyse alternative designs for the same production process. The emissions presented in Table 6.3 were obtained from a mass balance which was performed around the process as part of the IPC application for authorisation (HMIP, 1994c).

Table 6.3 Nitrobenzene production emission summary

Substance	Release	Units	Medium	Impact
Benzene	264	tpa	A	1.6
Nitrobenzene	7	tpa	A	2.2
Sulphuric Acid	24	tpa	A	1.3
CO_2	19,261	tpa	A	0.8
NO_x	3	tpa	A	1.9
Flash steam condensate (no chemicals)	11,787	tpa	W	0
Sodium nitrate	287	tpa	W	0.6
Calcium sulphate	37.7	tpa	L (OSD)	0.6
Iron sulphate sludge	34	tpa	L (OSD)	2.3

Any unreacted benzene which is not recycled to the reactor is discharged to the atmosphere along with releases of nitrobenzene which arise throughout the process. Sulphuric acid losses in the acid reconcentration stage are also vented to the atmosphere after passing through a series of scrubbers. The calcium and sodium salts arise in the washing of the nitrobenzene product and in the neutralisation of the sulphuric acid contaminated effluent from the scrubbers.

6.3 Formox process

This Formox process produces formalin, a 30-50 wt% aqueous solution of formaldehyde. The plant has a maximum production capacity of 63,000 tonnes per annum and operates 360 days per year (HMIP, 1994d).

Formaldehyde is produced via the vapour phase oxidation of methanol over a fixed metallic catalyst bed.

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[1\ atm]{115\ ^\circ C} CH_2O + H_2O$$

The schematic flowsheet of the process is shown in Figure 6.3. Methanol from bulk storage is injected into an air stream and the air-methanol mixture is vaporised and passed through two parallel processing trains. In these trains the feed mixture is passed over a hot catalyst where the exothermic oxidation reaction occurs and formaldehyde is produced. The formaldehyde is absorbed into formalin solution before being drawn off to product storage. Unreacted gases are recycled and the by-products together with some unreacted feed are discharged to the atmosphere after combustion in an incinerator.

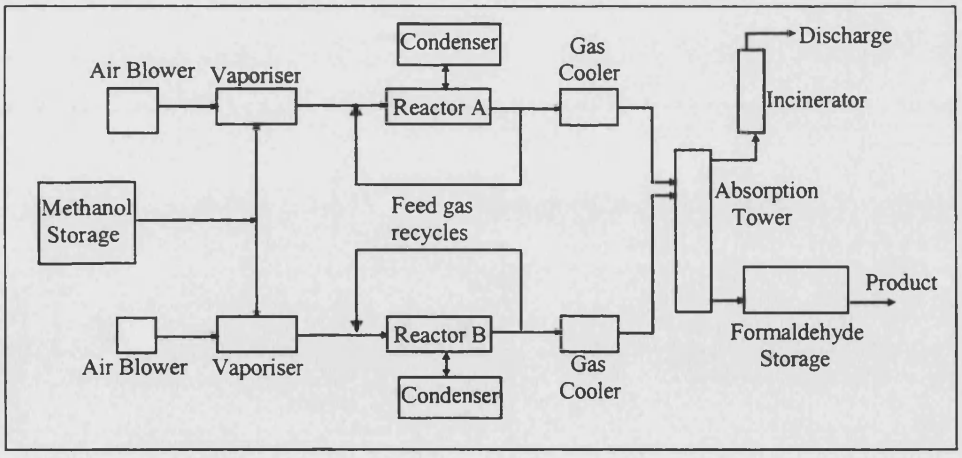

Figure 6.3 Formox process schematic diagram

There are two major sources of pollution which arise from the continuous operation of this plant, the most significant of which is the stack used to discharge the wastes

from the incinerator. The incinerator combusts the waste reaction gases which are bled off from the stream which is continuously recycled through the system. The second major source of pollution arises from fugitive emissions from tanks, pipelines and fittings. All the emissions listed in Table 6.4 are based on the 1994 production level of 22,031 tpa.

Table 6.4 Formox production emission summary

Substance	Release	Units	Medium	Impact
Formaldehyde	11.6	tpa	A	1.7
Methanol	13.7	tpa	A	1.5
VOC (Toluene)	0.26	tpa	A	1.8
NO_2	7.7	tpa	A	1.9

6.4 Paraxylene production

In this process 345,000 tonnes per annum of pure paraxylene is produced by isomerisation of a mixture of xylene isomers (meta, ortho and para)(HMIP, 1994e). A simple schematic for the process is shown in Figure 6.4. The isomerisation reactor consists of a fixed bed catalyst operated at moderate pressure over which superheated mixture of vaporised xylene isomers is passed. On average the fall off in reactor performance with time dictates regeneration of the catalyst once every three months.

Following the removal of the unreacted meta and ortho isomers by distillation the recovery of the paraxylene product is achieved by crystallisation of liquid paraxylene. The unreacted meta and otho isomers are recycled to the reactor. The distillation is followed by the separation of the solid paraxylene crystals using filters and centrifuges. High purity product is produced by pentane washing.

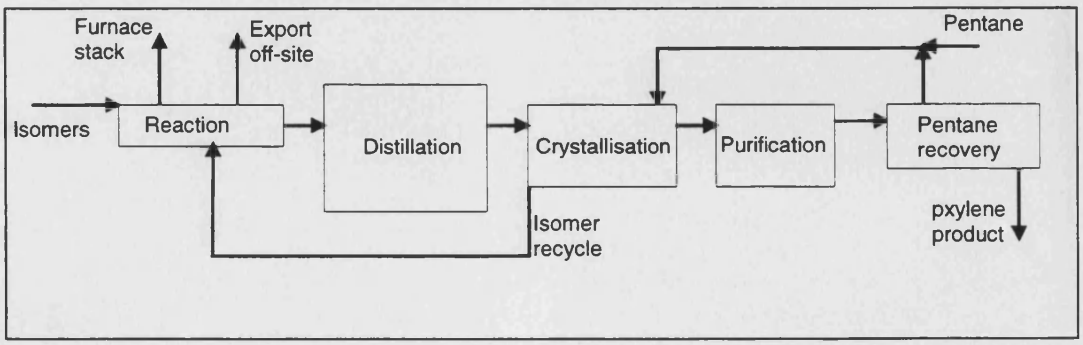

Figure 6.4 Paraxylene production process schematic diagram

The emissions from the reaction vessels are passed through a furnace before being discharged to the atmosphere as shown in Figure 6.4. Most of the emissions shown in Table 6.5 arise due to the venting of the by-products such as benzene and toluene and products in the later purification stages. The IPC authorisation does not indicate where the ethylene or chromium arise however it is likely that the chromium is used as a catalyst in the reactor and the ethylene is produced during the reaction stages.

Table 6.5 Paraxylene process emission summary

Substance	Release	Units	Medium	Impact
Benzene	31	tpa	A	1.6
Toluene	16	tpa	A	1.8
Pentane	124	tpa	A	1.0
Paraxylene	122	tpa	A	1.6
Ethylene	110	tpa	A	1.7
Chromium	5×10^{-3}	tpa	W	4.8

6.5 Hydrogen chloride production

This process manufactures anhydrous hydrogen chloride gas by the reaction of hydrogen and chlorine (HMIP, 1992b). The plant produces an aqueous solution containing 36% hydrochloric acid, has a maximum operating capacity of 111,111 tonnes per annum and operates for 333 days each year. A simplified schematic diagram of the process is shown in Figure 6.5. To produce the hydrogen chloride, gaseous hydrogen and chlorine are mixed under pressure and reacted together in an impregnated graphite combustion chamber.

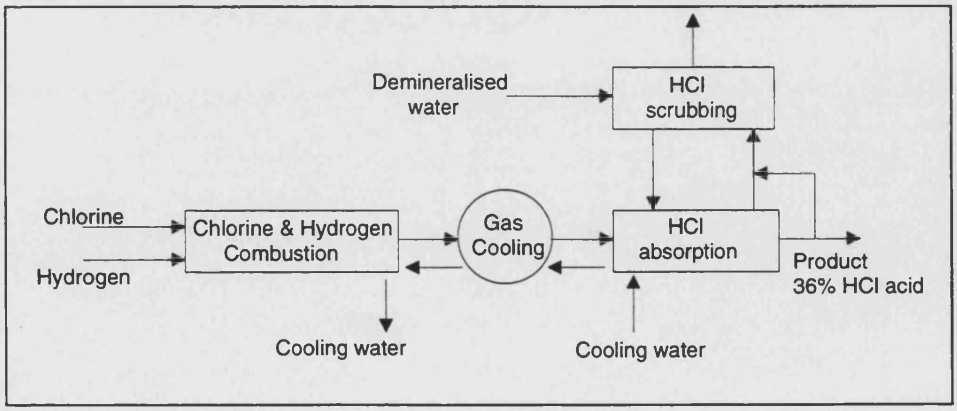

Figure 6.5 HCl production schematic diagram

A 5-10% molar excess of hydrogen is used in the reaction in order to ensure that no chlorine is present in the process downstream of the reactor. This reduces the risk of toxic effects and explosion. The hydrogen/chlorine flame in the reactor can reach temperatures of up to 2600°C and a cooling jacket is used to reduce its effects on the combustion chamber. The hydrogen chloride gas is then passed through a countercurrent isothermal falling film absorber. The gas passes upwards through the absorber and is continuously contacted with demineralised water and hydrochloric acid (21 wt%). The hydrochloric acid product (36%) leaves at the base of the absorber and the gases leaving the top are passed through a scrubber to remove most of the remaining hydrogen chloride. The effluent from this scrubbing process which may be either weakly acidic or weakly basic is discharged to the water system. The emission summary for the process is shown in Table 6.6.

Table 6.6 HCl production emission summary

Substance	Release	Units	Medium	Impact
Hydrogen	109.6	tpa	A	1.1
Water	29.6	tpa	A	0.2
Hydrogen Chloride	0.073	tpa	A	1.3
Chlorine	0.01	tpa	A	1.7
Mixed acid/caustic	180	tpa	W	1.7

6.6 Specialty organic chemicals

This plant is a continuously operated multi-product plant. The major product is 2-ethyl hexyl nitrate which is used as a diesel fuel additive (HMIP, 1994f). It is produced by nitrating 2-ethyl hexanol (octanol) using a mixture of concentrated nitric and sulphuric acids as shown in the first of the two schematic diagrams presented in Figure 6.6. The production rate for this operation is typically 5000 to 15000 tonnes per annum of product depending on demand.

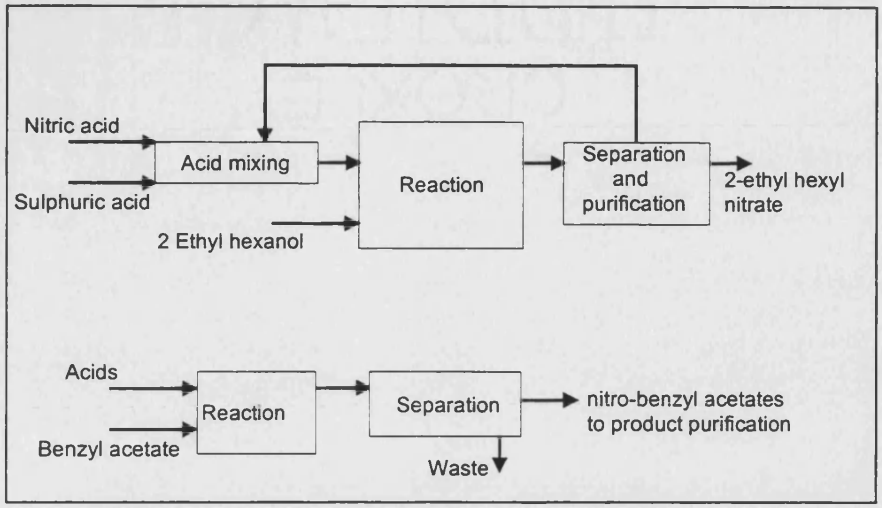

Figure 6.6 Specialty chemicals production schematic diagram

The plant is also used to produce nitro-benzyl acetates by the nitration of benzyl acetate as shown in the second schematic in Figure 6.6. The production rate of these nitro-benzyl acetates is 50 to 100 tonnes per annum. The product which is a mixture of isomers is sent to a separate batch plant for separation and purification. The separate batch purification process was not considered within the scope of this analysis. The emissions that are presented in Table 6.7 arise from the two reaction processes and the purification of the 2-ethyl hexyl nitrate. Most of the pollutants are heavy metals which are used as catalysts throughout the production processes. A large quantity of sulphuric acid is also discharged following its use as a catalyst in the nitration process.

Table 6.7 Specialty chemicals production emission summary

Substance	Release	Units	Medium	Impact
NOx	0.32	tpa	A	1.9
Toluene	0.01	tpa	A	1.8
Cadmium	8×10^{-5}	tpa	W	4.7
Chromium	6.6×10^{-3}	tpa	W	4.8
Copper	2.7×10^{-3}	tpa	W	3.3
Lead	1.6×10^{-3}	tpa	W	4.7
Mercury	1.3×10^{-5}	tpa	W	4.2
Nickel	5.3×10^{-3}	tpa	W	4.7
Nitric acid	98.6	tpa	W	1.6
Sulphuric acid	1,682	tpa	W	1.3
Zinc	1.9×10^{-2}	tpa	W	3.1

6.7 Industrial boiler plants

Four different operators of industrial boilers were selected for testing EniVal. The operation of boilers involves the combustion of fuel to produce energy, waste gases and particulates. Boilers are well suited for the preliminary, simple analyses using EniVal because there are only two or three common emissions all of which are discharged to the same medium (the atmosphere). Table 6.8 presents a list of the types of boilers that have been studied and the typical fuels that they use.

Table 6.8 Summary of industrial boilers

Operator	No. of units	Type	Thermal rating	Fuel
A (HMIP, 1991)	3	Industrial boilers	48 MWth each	Either natural gas or heavy fuel oil
B (HMIP, 1992c)	1	Industrial boiler	37.5 MWth	Heavy fuel oil
	1	Industrial boiler	49.5 MWth	Heavy fuel oil and natural gas
	1	Industrial boiler	12.2 MWth	Heavy fuel oil or polyphenyls by-product (PPB)
C (HMIP, 1993b)	3	Industrial boilers	63.8 MWth each	Refinery fuel gas and residual fuel oil
D (HMIP, 1993c)	1	Waste heat boiler	24.2 MWth	Gas or gas oil
	1	Industrial boiler	32 MWth	Heavy fuel oil
	1	Industrial boiler	32 MWth	Gas
	2	Turbines	14 MWth each	Gas

Tables 6.9 to 6.12 provide summaries of the emissions from the boilers. As shown the only emissions which are reported for the industrial boilers are sulphur dioxide, nitrogen oxides and particulates all of which are discharged to the atmosphere. The different boiler plants were rated as shown in Tables 6.9 to 6.12 according to their actual thermal output when operating 333 days per year.

Table 6.9 Boiler plant A emission summary

Total thermal output: 1152000 MWth				
Substance	Release	Units	Medium	Impact
SO_2	2193	tpa	A	1.7
NOx	268	tpa	A	1.9
Particulates	221	tpa	A	1.1

Table 6.10 Boiler plant B emission summary

Total thermal output: 793600 MWth				
Substance	Release	Units	Medium	Impact
SO_2	11760	kgpa	A	1.7
NOx	39504	kgpa	A	1.9
Particulates	2664	kgpa	A	1.1

Table 6.11 Boiler plant C emission summary

Total thermal output: 1531200 MWth				
Substance	Release	Units	Medium	Impact
SO_2	547	tpa	A	1.7
NOx	1095	tpa	A	1.9

Table 6.12 Boiler plant D emission summary

Total thermal output: 928000 MWth				
Substance	Release	Units	Medium	Impact
SO_2	316	tpa	A	1.7
NOx	124	tpa	A	1.9
Particulates	10	tpa	A	1.1

6.8 Cement clinker production

A recent study of two cement clinker plants was used to show the limitations of the HMIP BPEO selection process (ENDS, 1995). Castle Cement's study involved analysing the discharges from two plants, one using the traditional wet process and the other operating with the more modern dry process and showed how the HMIP's IEI favoured the process with the greater emissions.

Nearly all cement clinker is produced in large rotary kiln systems. These kilns are countercurrent heating devices which are slightly inclined to the horizontal so that the material fed into the upper end travels slowly by gravity to be discharged onto the clinker cooler at the discharge end. In the wet process the raw materials are fed to the kiln in the form of a slurry. Most of the liquid is evaporated in the upper stages of the kiln leaving a drier material for the later reaction stages. The dry process on the other hand utilises a dry kiln feed rather than a slurry and often incorporates the

use of cyclones. These cyclones which contact the dry pulverised feed with hot gases are used to separate and preheat the feed before it is introduced to the kiln at 800-900°C. It is the use of these preheat cyclones which increases the efficiency of the overall clinkering process and thus reduces the emissions as shown in Tables 6.13 and 6.14. Both of the clinker processes presented here are operated at 750000 tonnes of clinker per annum.

Table 6.13 Conventional wet cement clinker process emission summary

Substance	Release	Units	Medium	Impact
SO_2	22,005	tpa	A	1.7
NOx	35,280	tpa	A	1.9
Particulates	147	tpa	A	1.1
CO_2	783,000	tpa	A	0.8

Table 6.14 Modern dry cement clinker process emission summary

Substance	Release	Units	Medium	Impact
SO_2	13,125	tpa	A	1.7
NOx	21,000	tpa	A	1.9
Particulates	87	tpa	A	1.1
CO_2	578,250	tpa	A	0.8

6.8 Summary

This chapter has presented an overview of the 12 processes which have been used to develop EniVal. The emission data which are presented for each of the process have been taken from the actual process operating data which are available through the public registers of IPC authorisations in the UK. These data have been used to develop the techniques which are incorporated into EniVal to combine the pollutant property data from the parameters presented in Chapter 4 with the pollutant discharge data. The development of these combination techniques is presented in detail in Chapter 7.

Chapter 7

Combining impact and mass scores

The overall impact score obtained as described in Chapter 5 represents the potential impact that a given pollutant can have when discharged to the environment. However as discussed in Chapter 2, neither a simple impact score nor a single load factor index is sufficient to describe fully the total environmental impact. A combination of the impact scores for each of the pollutants and a load factor index is required.

Figure 7.1 shows the range of impact and discharge data which exists for the 12 industrial processes described in Chapter 6. The impact and discharge data are taken from Tables 6.2 to 6.14. In Figure 7.1 the discharge ratio is defined as the quantity of a chemical discharged from a process divided by the production level for that process. As shown there is a wide variation in the spread of values with some pollutants having high impacts and low discharges and others with low impacts and high discharges. The majority of the pollutants have impacts between 1 and 2 and discharge ratios of greater than 0.1. The problem is to find a method of combining these two sets of data to produce an overall impact score for each process.

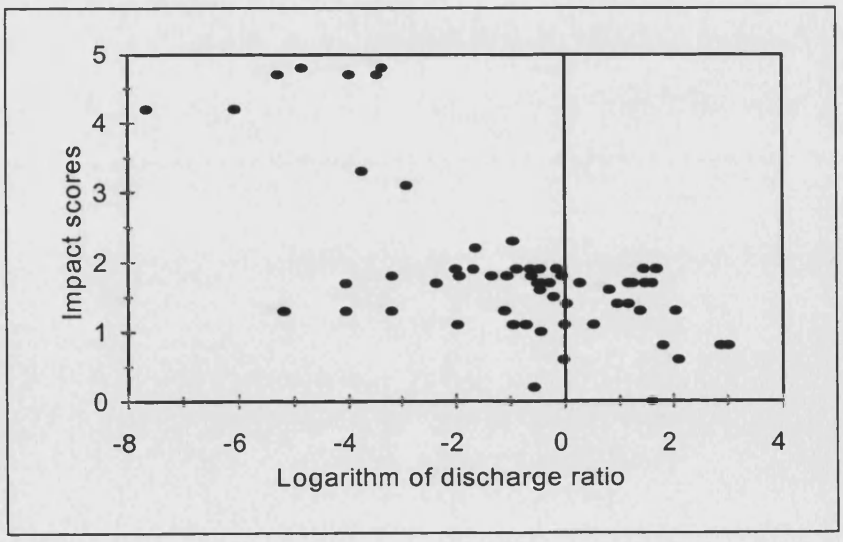

Figure 7.1 Impact and discharge data for 12 industrial processes

Section 7.1 describes five alternative methods for combining impact and mass data that were investigated for EniVal. The alternatives were assessed to determine which provided the most appropriate set of impact scores, on the basis of:

1. the range and spread of overall impact scores;
2. the effects of errors in raw data on the overall impact; and
3. the sensitivity of the combination technique to changes in process data.

The range and spread of overall impact scores is discussed qualitatively in section 7.1. An initial study of the spread of values was made using the variance and standard deviation of the values. However due to discontinuities in the data caused by the very high emissions from the cement processes this analysis could not be performed consistently across the alternative combination methods which were analysed. Thus a descriptive analysis was performed for which the objectives were to obtain a reasonable spread of values, a reasonably even distribution between the minimum and maximum values and a clear distinction between the overall impact values for individual processes.

Section 7.2 discusses the interaction of the errors in the raw data and the effects of these errors on the overall values while section 7.3 investigates the sensitivity of EniVal to modifications to the process. From these analyses a final selection was made for the combination of impact scores and discharge data.

7.1 Combination options

Five options were chosen for the combination of the impact scores with the discharge data. EniVal incorporates both the quantity (Q_i) of the pollutant i which is discharged and the overall production rate (Q_T) of the process. The inclusion of the total production rate means that EniVal can be used to compare processes of different capacities. For each option the overall impact scores and the ELF values for each of the processes are compared. The ELF values for the boilers are different to those for the chemical processes as they are based on energy output rather than mass of product. This fact should be noted when comparing these values.

While the impact scores which were developed in Chapter 6 all range between 0 and 10, the discharge data is bounded only by the operating limits of the process. Thus the final impact scores for each form of EniVal will not have a set range of values. The scores are only useful as a comparison of the relative environmental impact of different processes within the bounds of the same analysis technique. The five alternative combinations of impact and mass evaluated are listed in Table 7.1. The log discharge ratio used in Options 2, 4 and 5 is defined as

$$\text{Log discharge ratio} = \frac{\log(Q_i)}{\log(Q_T)} \qquad (7.1)$$

All the logarithm functions incorporated in Options 2 to 4 are to the base 10.

Table 7.1 Impact-quantity combinations

Option	Formula	Description
1	$\sum_i \left(I_i \times \frac{Q_i}{Q_T} \right)$	Impact score multiplied by discharge ratio
2	$\sum_i \left(I_i \times \frac{\log(Q_i)}{\log(Q_T)} \right)$	Impact score multiplied by log discharge ratio
3	$\sum_i \left(10^{I_i} \times \frac{Q_i}{Q_T} \right)$	Inverse log of the impact score multiplied by the discharge ratio
4	$\sum_i \left(10^{I_i} \times \frac{\log(Q_i)}{\log(Q_T)} \right)$	Inverse log of the impact score multiplied by the log discharge ratio
5	$\sum_i \left(e^{I_i} \times \frac{\ln(Q_i)}{\ln(Q_T)} \right)$	Exponential of the impact score multiplied by the natural log discharge ratio

Option 1 was the initial combination studied due to its simplicity. The formula was applied to the discharge data for the 12 processes presented in Chapter 6 to examine the suitability of the option for determining the overall impact of a chemical process.

The range of values for Option 1 is given in Table 7.2. As shown, the two cement clinker plants have impact scores (with Option 1) which are much greater than those for the other processes causing a discontinuity in the overall range of data. The relatively high impact scores are due to the very high discharge ratio values for the CO_2 emissions compared with the production levels of clinker. These ratio values

are high due to the elevated temperatures and long residence times required in the clinker kilns. To produce these operating conditions large amounts of fossil fuels are burnt which produce high levels of CO_2. Seven of the remaining ten processes were scored with total impacts between 0.1 and 4.5, which is a relatively narrow range of values making it difficult to distinguish between processes.

The impact scores for Option 1 do not reflect the pattern shown by the ELF values due to the combination of the discharge information from the ELF and the environmental impact parameters. Similar trends are shown between Option 1 and the ELF for the boilers as these involve only a small number of pollutants with similar impacts and the influence of the individual impact scores is minimal.

Due to the limited range and the uneven spread of the values provided by Option 1, other methods (Options 2 to 5) were investigated. These methods were designed to increase the contribution of the impact scores to the overall EniVal values relative to the contribution of the discharge ratio, thus reducing the problem of the discontinuities shown in Option 1.

Table 7.2 Option 1 total impacts : $\sum_i \left(I_i \times \frac{Q_i}{Q_T} \right)$

Process	Total impact	ELF
Boiler B	0.1	0.07
Boiler D	1.0	0.5
Paraxylene	1.6	0.001
Boiler C	2.3	1.1
Formox	2.7	0.002
Hydrogen chloride	4.0	0.003
Boiler A	4.5	2.3
Ethyl chloride	54	0.05
Nitrobenzene	104	0.002
Specialty chemicals	150	0.1
Cement clinker (dry)	770	0.8
Cement clinker (wet)	1080	1.1

Option 2 reduces the effect of the discharge ratio by incorporating the logarithms of the quantities. For the discharge ratio the logarithm functions reduce the possible range of values from the almost unlimited range for the standard discharge ratio to

values which are comparable to the impact scores. This would reduce the extent of the effects of relatively high discharge ratios such as those present in the cement clinker process. However by reducing the range of values for the discharge ratios the overall range of values calculated by EniVal is also limited, even more so than for Option 1. This is shown in Table 7.3 where all the impact scores for all 12 processes range between the values of 3.0 and 9.2. The ELF values for the combustion processes no longer match the EniVal scores due to the increased relative effect of the individual impact scores on the overall impact values.

Table 7.3 Option 2 total impacts : $\sum_i \left(I_i \times \frac{\log(Q_i)}{\log(Q_T)} \right)$

Process	Total impact	ELF
Ethyl chloride	3.7	0.05
Boiler C	4.0	1.1
Hydrogen chloride	4.0	0.003
Boiler D	4.5	0.5
Boiler B	4.6	0.07
Boiler A	5.0	2.3
Formox	6.0	0.002
Specialty chemicals	6.3	0.1
Paraxylene	6.5	0.001
Cement clinker (dry)	7.4	0.8
Cement clinker (wet)	7.6	1.1
Nitrobenzene	9.2	0.002

Instead of limiting the range of possible discharge ratios using the logarithms of the quantities, Option 3 utilises the inverse logarithm of the impact scores in order to match the impact scores to the ratios, rather than vice versa. With Option 3, the contribution of the impact scores to the overall EniVal is no longer a value between 0 and 10, but a value between 1 and 1×10^{10}. This contribution results in a much greater range and more even spread of values of EniVal for the processes studied as shown in Table 7.4. With the exception of the nitrobenzene process, the ELF values reflect the order of the chemical processes as indicated by the values for Option 3. The nitrobenzene process has a large discharge of sulphuric acid which has a relatively high impact and this results in a much greater overall impact score using Option 3 compared to the ELF which only uses the discharge data. This indicates that Option 3 does reflect both the individual impact scores and the discharge data.

Table 7.4 Option 3 total impacts : $\sum_i \left(10^{I_i} \times \frac{Q_i}{Q_T} \right)$

Process	Total impact	ELF
Boiler B	9.9	0.07
Paraxylene	29	0.001
Boiler D	57	0.5
Hydrogen chloride	107	0.003
Formox	110	0.002
Boiler C	160	1.1
Boiler A	230	2.3
Ethyl chloride	630	0.05
Nitrobenzene	870	0.002
Specialty chemicals	1300	0.1
Cement clinker (dry)	12000	0.8
Cement clinker (wet)	19000	1.1

Following the more successful results obtained using Option 3, it was decided to examine accentuating the effects of the impact scores whilst simultaneously suppressing the contribution from the discharge ratio. Thus Option 4 utilises the inverse logarithm of the impact scores and the ratio of the logarithm of the quantities.

The results for Option 4 which are presented in Table 7.5 show that once again there is a good spread of values which can be used to distinguish between the impacts of different processes. An example of this is for the specialty chemicals production which has the highest impact score due to its discharges of pollutants with high impacts (e.g. heavy metals) and high discharge ratios (e.g. sulphuric acid). Table 7.5 also shows that the range of values has been reduced compared with those shown in Table 7.4 for Option 3, due to the effect of the use of logarithm functions in the discharge ratio.

The order of processes indicated by Option 4 is completely different for all processes to that shown using the ELF. Option 4 accentuates the effects of the individual impact scores and minimises the contribution of the discharge data. Option 4 reflects predominantly the individual impact scores while the ELF only utilises the discharge data. Thus these alternatives (Option 4 and ELF) represent the two extremes of the analysis and not an effective combination of the two sets of data.

Table 7.5 Option 4 total impacts : $\sum_i \left(10^{I_i} \times \frac{\log(Q_i)}{\log(Q_T)} \right)$

Process	Total impact	ELF
Ethyl chloride	96	0.05
Hydrogen chloride	101	0.003
Boiler B	208	0.07
Paraxylene	240	0.001
Boiler D	245	0.5
Boiler C	258	1.1
Formox	261	0.002
Boiler A	267	2.3
Cement clinker (dry)	353	0.8
Cement clinker (wet)	360	1.1
Nitrobenzene	483	0.002
Specialty chemicals	588	0.1

The fifth option which was investigated involved the use of the exponential of the impact scores combined with the natural logarithm of the quantities. This option was considered in order to determine the effect of increasing the contribution of the impact scores but to a lesser extent than by using the inverse logarithm to base 10. The results shown in Table 7.6 indicate that the use of the exponential does not provide a sufficiently large spread of values. The results from the ELF compared to Option 5 are similar to those for Option 4 although Option 5 incorporates a slightly smaller contribution from the individual impact scores due to the use of the natural logarithm.

Table 7.6 Option 5 total impacts : $\sum_i \left(e^{I_i} \times \frac{\ln(Q_i)}{\ln(Q_T)} \right)$

Process	Total impact	ELF
Hydrogen chloride	13	0.003
Boiler B	14	0.07
Ethyl chloride	15	0.05
Boiler C	16	1.1
Boiler D	17	0.5
Boiler A	19	2.3
Formox	21	0.002
Paraxylene	21	0.001
Specialty chemicals	25	0.1
Cement clinker (dry)	26	0.8
Cement clinker (wet)	27	1.1
Nitrobenzene	37	0.002

From the five alternative combinations of impact scores and discharge ratios which have been presented in section 7.1, Options 3 and 4 yield the greatest ranges of values and provide clear distinctions between the overall impacts of different processes. Option 4 clearly groups the boilers and clinker plants together, all of which have the same types of pollutants and involve combustion processes. Also the chemical plants have greater impacts when analysed using Option 4 which reflects the greater variety of polluting chemicals which are discharged to all three environmental media. The specialty chemicals production receives the highest overall impact score as expected with its large emissions of sulphuric acid and the large number of heavy metal discharges as described in Chapter 6. The comparison of Option 4 to the ELF indicated that Option 4 may place too much emphasis on the individual impact scores thus swamping any effect from the discharge data. Option 3 appeared to provide a more balanced combination of impact and discharge data relative to the ELF.

On the basis of the discussion in this section Option 4 is the best alternative, followed by Option 3. Options 1, 2 and 5 have been discounted due to the very limited and disjointed ranges of impact values provided. From these initial findings, Options 3 and 4 were chosen for further analysis to investigate the effects of errors on the combination techniques and the sensitivity of the formulae to changes in the data.

7.2 Error Analysis

An error analysis was performed to study how errors in the raw data accumulate throughout the tree structure to affect the final overall impact score. Errors can arise in many ways in the analysis of the environmental impact of a given process, with the major sources coming from the raw data which is used to score the impact of each chemical. An error analysis has been performed to show how these errors increase as the parameter scores are combined up through the tree. The results shown in Table 7.7 and Appendix F are for the worst case scenario where it is assumed that the maximum possible error for the scores for all the relevant parameters ($\pm$ 1) will exist simultaneously. In practice it is unlikely that every parameter would be so inaccurate. For simplicity the assumption is made that the 28 parameters are linearly

independent, however in practice it is recognised that they are not truly independent values.

Table 7.7 Impact tree error analysis results

System	Short-term impact error	Long-term impact error
Atmosphere	3 %	9 %
Water	3 %	8 %
Soil	3 %	8 %

The errors shown in Table 7.7 were then incorporated into the analysis of 8 of the 12 processes discussed in Chapter 6 (the cement plants were used to represent the combustion processes) to determine the effects of these worst-case errors on the overall impact scores. The errors which were transferred to the total impacts for each of the processes are shown in Table 7.8. There is a '+' error and a '-' error for each process due to the effect of the inverse logarithm of the impact which is incorporated into both Options 3 and 4. When the impact score changes by the percentage shown in Table 7.7 the contribution changes from 10^{Ii} to $10^{(Ii \pm \delta Ii)}$. Accordingly the relative impact difference varies with the sign of the error.

Table 7.8 Error analysis results for processes

	Option 3		Option 4	
Process	+	-	+	-
Paraxylene	23%	19%	37%	26%
Formox	19%	16%	20%	17%
Nitrobenzene	26%	20%	25%	20%
Hydrogen chloride	16%	14%	17%	14%
Ethyl chloride	18%	15%	20%	16%
Specialty chemicals	19%	16%	38%	27%
Cement A	15%	13%	22%	20%
Cement B	16%	14%	22%	18%
Average	19%	16%	25%	20%

Table 7.8 shows that for the 8 processes studied, the errors for Option 3 are significantly less than those for Option 4. This was expected due to the effect of the discharge ratio in Option 3 which utilises pollutant quantities rather than the logarithm of the quantities. As EniVal is designed to be used as a preliminary screening tool, an accuracy to within 40% is still acceptable. However the reduced errors in Option 3 (with a maximum error of 26% for the cases studied) are more in

line with the accuracy associated with preliminary cost estimations (± 30%) which are used to make choices between design alternatives (Coulson and Richardson, 1983). The overall impact values for the design alternatives could be compared with preliminary cost estimates to determine the Best Practicable Environmental Option (BPEO). Thus the impact scores and costs must have similar accuracy to ensure a valid comparison. From the cases studied above, Option 3 was shown to be more favourable with respect to errors than Option 4 for the determination of the BPEO.

7.3 Sensitivity analysis

Another major issue of concern when comparing the relative environmental impacts of different processes is the sensitivity of EniVal to changes in the quantities of the discharge of pollutants which may arise due to process alterations. EniVal has been designed for use in the analysis of retrofits as well as for the selection of new designs so it is important to select the best alternative from Options 3 and 4 for this purpose.

Two of the industrial processes described in Chapter 6 were analysed separately to determine the sensitivity of the two retained options for EniVal to variations in discharge data. These two processes were the specialty chemicals plant and the paraxylene production. In each of these processes several pollutants were selected for further study according to whether they had high impact scores or high discharge ratios. The discharge quantities of these chemicals were then altered and the resulting changes in total impact were noted. Figure 7.2 shows the effects on EniVal for the specialty chemicals manufacture of reducing the discharge of sulphuric acid.

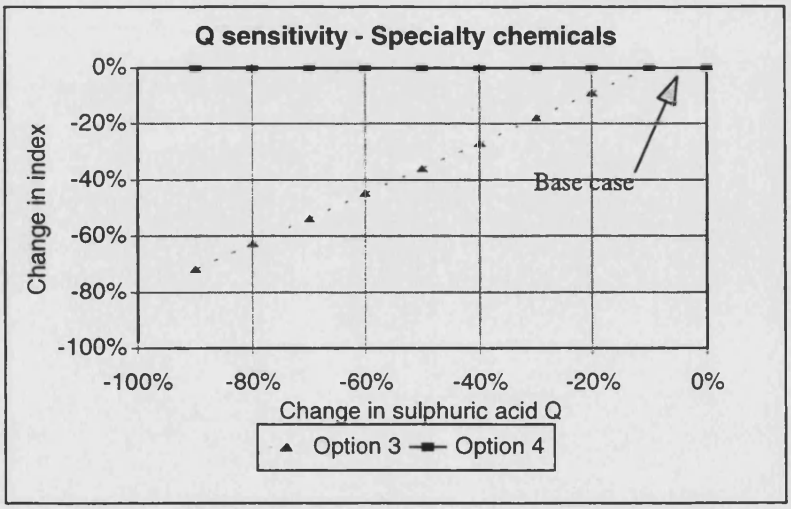

Figure 7.2 Sensitivity analysis for pollutant with large discharge and medium impact

The effects of reducing the emission of nickel for the same process are shown in Figure 7.3. In this case although nickel has a relatively high impact it is present in small quantities.

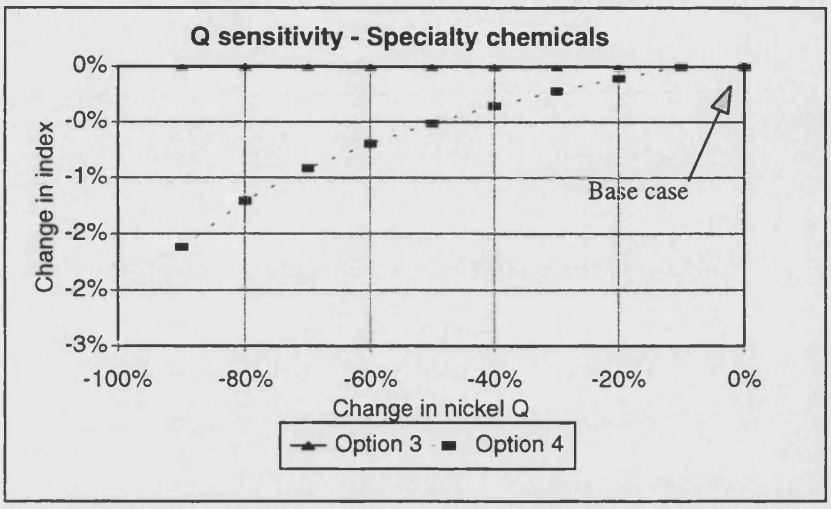

Figure 7.3 Sensitivity analysis for pollutant with small discharge and high impact

The third case for the specialty chemicals manufacture also investigates the effects of reducing the emissions of a high impact pollutant with a small discharge. Figure 7.4 shows the changes in the values of EniVal when utilising Options 3 and 4 for zinc. The relevant discharge and impact data for zinc can be found in Table 6.7.

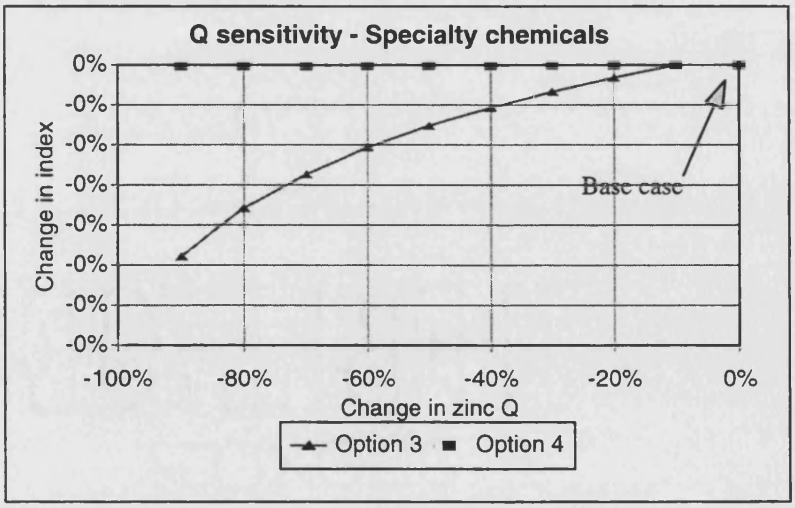

Figure 7.4 Sensitivity analysis for pollutant with small discharge and high impact

The second process which was analysed was the production of paraxylene as described in Chapter 6, section 6.4. Figure 7.5 shows the performance of Options 3 and 4 for variations in the emission of chromium.

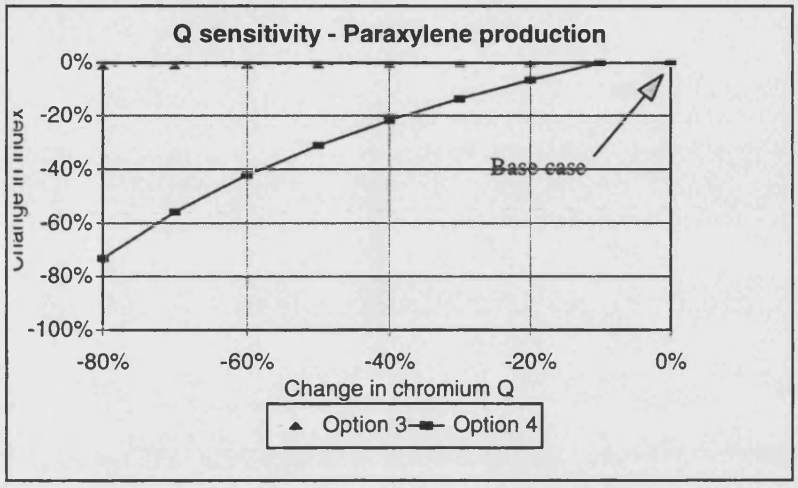

Figure 7.5 Sensitivity analysis for pollutant with small discharge and high impact

Figure 7.6 shows the results for the second study involving the paraxylene production. In this case the emissions of the product, paraxylene were studied. For this process paraxylene is a pollutant with a high discharge and a medium environmental impact.

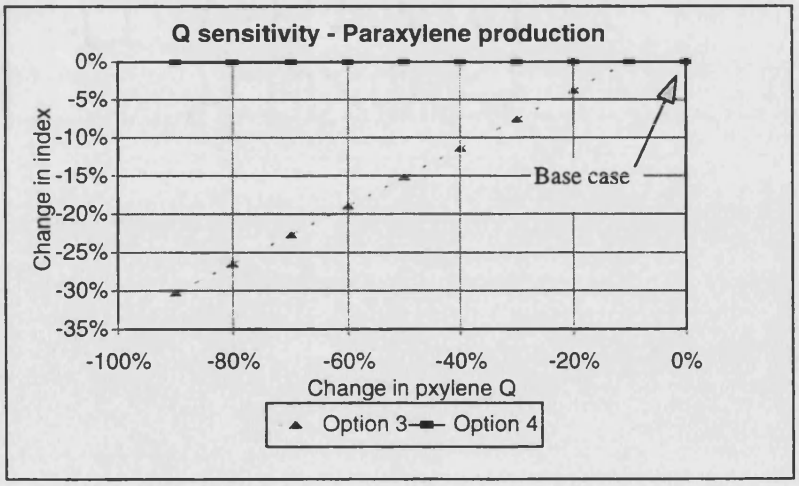

Figure 7.6 Sensitivity analysis for pollutant with large discharge and medium impact

The results shown in Figures 7.2 to 7.6 show that reducing the discharge of pollutants with high impacts and low emissions has little effect on EniVal based on Option 3, while the reduction of pollutants with high emissions and lower impacts has a much greater effect. The opposite effects were observed for Option 4.

When the discharge of a pollutant is reduced by an amount δQ, the contribution to the overall impact for that pollutant changes by different amounts for Options 3 and 4 as shown in Table 7.9.

Table 7.9 Sensitivity of EniVal to dicharge ratio

Option	Fractional contribution to EniVal
3	$\times \left(\frac{Q - \delta Q}{Q} \right)$
4	$\times \left[\frac{\log(Q - \delta Q)}{\log(Q)} \right]$

For a 50% reduction in the discharge of a pollutant, its contribution to EniVal based on Option 3 will also be reduced by 50%. However for the same pollutant and EniVal based on Option 4, the reduction in the overall impact will change according to the discharge quantity of the pollutant as shown in Table 7.10. For the same percentage reduction in the discharge of a pollutant, the contribution of that pollutant to the overall value of EniVal decreases as the discharge quantity increases. Thus Option 4 will not provide a true indication of the effects of process retrofits as it is biased against pollutants which are discharged in large quantities.

Table 7.10 Sensitivity of EniVal to the discharge ratio for Option 4

Q	Reduction in Q (50%)	Reduction in contribution to EniVal (Option 4)
10	5	30%
100	50	15%
1,000	500	10%
10,000	5,000	7.5%

7.4 Selection of the final form of EniVal

In sections 7.1 to 7.3 the various ways of combining the discharge data from a given process with the environmental impact of each pollutant have been analysed. In section 7.1 five alternative options were identified involving the use of various combinations of logarithm and inverse logarithm functions. From the analysis of these five options, two were identified as providing a sufficient range of values for the processes studied and providing a clear distinction between processes. These were Option 3 (inverse logarithm of the impact score multiplied by the discharge ratio) and Option 4 (inverse logarithm of the impact score multiplied by the logarithm discharge ratio).

Options 3 and 4 were then assessed further in section 7.2 to investigate the effects of errors in the impact data on the overall EniVal values. For the worst case error scenario, both options were able to provide overall impact scores with an accuracy of approximately ± 40%. However Option 3 had the smallest errors with a maximum of + 26% for the 8 processes studied.

The two options were then analysed in section 7.3 to study the effects of reducing the emissions of various pollutants on the overall EniVal values. This analysis showed that Option 4 was biased against pollutants with very high discharges. For the same percentage reduction in discharge the decrease in the contribution of a pollutant with a high emission was less than that for a pollutant with a small discharge. On this basis Option 4 is unacceptable for use in EniVal. Reductions in the discharges of pollutants with very low impacts tended to have minimal effects on Option 3. However this is to be expected where the amounts being released are so small (as for most of the heavy metals in the specialty chemicals production). Thus Option 3 was selected as being the best of the five alternatives presented in Table 7.1. The final form of EniVal is shown in equation (7.2).

$$\text{EniVal} = \sum_{i} 10^{I_i} \times \left(\frac{Q_i}{Q_T} \right) \qquad (7.2)$$

where

I is the impact score;

Q is the discharge quantity;

Q_T is the production capacity; and

i represents each pollutant in the process.

In Chapter 8 two of the industrial processes are used to test the value of EniVal as defined in equation (7.2). Two case studies are presented, the first of which investigates the effects of process modifications on the environmental performance of the Formox process. The second case study analyses two alternative designs for the production of nitrobenzene.

Chapter 8

Using EniVal

The development of EniVal as a tool which can be used to assess the relative environmental impact of alternative process designs has been presented in Chapters 3 to 7. In this chapter the implementation of EniVal as a stand alone computer-based tool will be discussed. This chapter also presents two case studies which show the use of EniVal to analyse process modifications and changes to the Formox process and to the production of nitrobenzene.

8.1 Computer implementation

The calculation of the overall impact scores for a process using EniVal can require large amounts of data related to both the process and the pollutants. Processing of these data is most easily achieved using a computer which can store the data, carry out the required large number of computations efficiently and present the results in an easily understood manner. Several alternatives were investigated for the presentation of EniVal as a computer-based tool including spreadsheets, databases and programming packages.

8.1.1 Choice of development package

EniVal has been implemented as a stand-alone computer program running under Windows™ using Microsoft® Visual Basic™. The interactive graphical user interface which can be easily created using Visual Basic™ ensures that EniVal is accessible to design engineers including those with minimal knowledge of computers and/or environmental impact analysis. The program was designed to operate as an independent executable programme on a PC so that it can be made readily available in a design office to engineers requiring the data and knowledge needed for assessing the environmental impact of chemical processes.

Visual Basic™ was chosen as the best alternative for EniVal as it provides a relatively simple method of constructing an independent computer program (executable file) that can be applied in any design situation. Spreadsheets and databases require the user to install the extensive software that must accompany the application before any

analysis can be performed. The extra software can consume large amounts of computer resources and may require additional training for new users.

As Visual Basic™ enables the construction of an executable program that operates under Windows, users need only be familiar with the Windows operating environment. As Feldman et al (1993) identified, "with Visual Basic™ you can write full-fledged Windows applications with relative ease". Yager (1993) also identified that "Visual Basic™ simplified working in Windows and gave the rewards of custom programming to even occasional programmers. It's still the quickest, most painless way to create professional looking Windows applications". More recently Hettler (1996) reinforced the message by commenting that "Visual Basic™ has always been a powerful tool for developing Windows applications".

The use of a visual programming package as opposed to a procedural one allows for more user control in the analysis of environmental impact. Feldman et al (1993) stated that "the essence of a procedural language is that the program is in control directing the logic flow procedurally through the program from the beginning to the end". They also identified that "Visual Basic™ is event-driven, that is program instructions execute only when a particular event calls that section of code into action". Thus the user is in full control of the analysis and within limits can dictate to the program which steps they wish to perform and in which order.

The presentation of the tree structure of EniVal and the analysis data within it is described in section 8.1.2 along with the advantages of using a graphical technique to display the impact data. A disk with copies of the relevant executable files is included at the end of this thesis along with simple instructions for use.

8.1.2 Presentation

The user's first interaction with EniVal begins with the introductory screen shown in Figure 8.1. This screen provides general information about the generation of EniVal and prompts the user to begin a new analysis by selecting the desired option be 'clicking' on the text or on the corresponding set of "traffic lights". On the introductory screen, the user may only choose an alternative for which the "traffic

lights" are green or red. An amber light indicates that more information is required before the user can gain access to that area of EniVal.

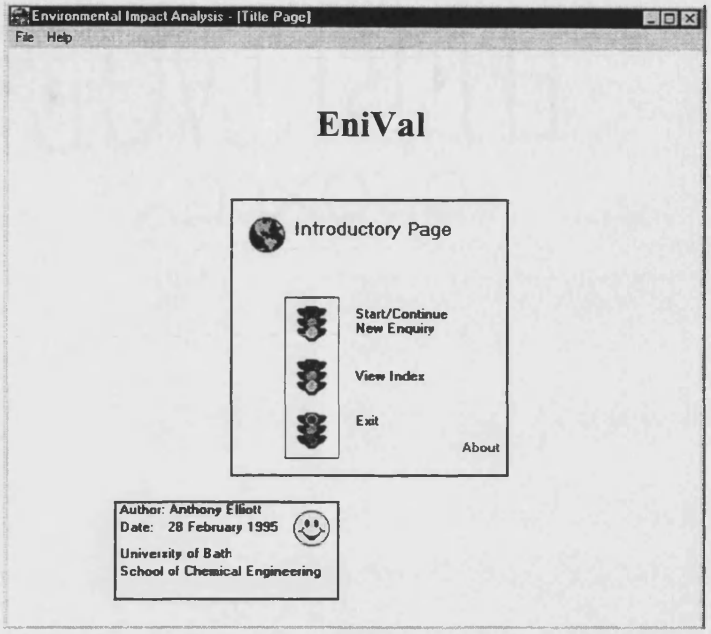

Figure 8.1 Introductory screen for EniVal

When the 'Start/Continue New Enquiry' option is selected, the user is prompted to enter a variety of information about a process through a number of screens displaying text boxes and selection lists. The type of information which is required includes the name of the process, the annual production capacity and a list of all the chemicals which are discharged. This information can be saved as a text file for future investigations of the same process.

The user is then asked to identify all of the pollutants from the process either by entering the names of new pollutants or by selecting the appropriate chemical from the list of those saved in the data file. New chemicals can be saved to the data files as required. At this stage the user can also enter details relating to the site of the process including the location factors described in Chapter 4 and the relevant volume fractions for the environmental media (atmosphere, water and soil).

Once the pollutants have been selected for the analysis the user must input all of the raw data for the parameters required for each of the chemicals. If the pollutant was selected from a data file then these data have been previously entered and saved.

Figure 8.2 shows that as data is entered on a data sheet, the scores for the parameters are updated automatically as shown in the right-hand columns.

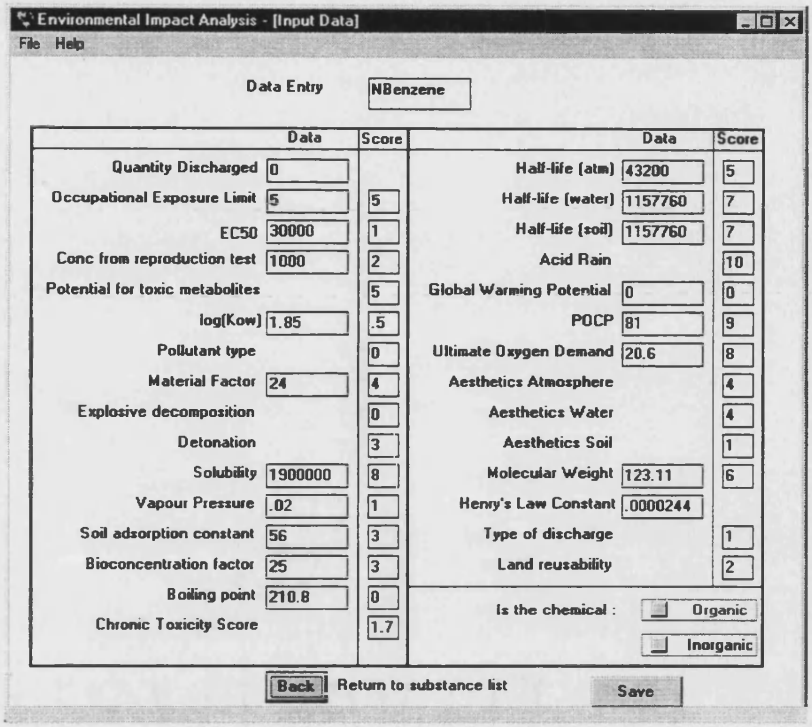

Figure 8.2 Data entry screen for nitrobenzene

Once the datasheets have been completed for all the pollutants the user can return to the introductory screen shown in Figure 8.1 where the 'View Index' "traffic lights" will have changed from amber to green. The user can now access the results of the analysis of their process. The results are displayed on the tree structure of EniVal described in Chapter 3 and shown in Figure G.1 in Appendix G (lift out sheet). A sample of the first screen showing the overall impact scores for the base case of the Formox process studied in section 8.2 is shown in Figure 8.3. The graphical approach to the development of Windows applications allows for a simple and easily understood representation of the result of the analyses. As shown the user also has the option of generating and printing a report for the analysis which contains all the impact scores and quantities of each pollutant and the overall impact.

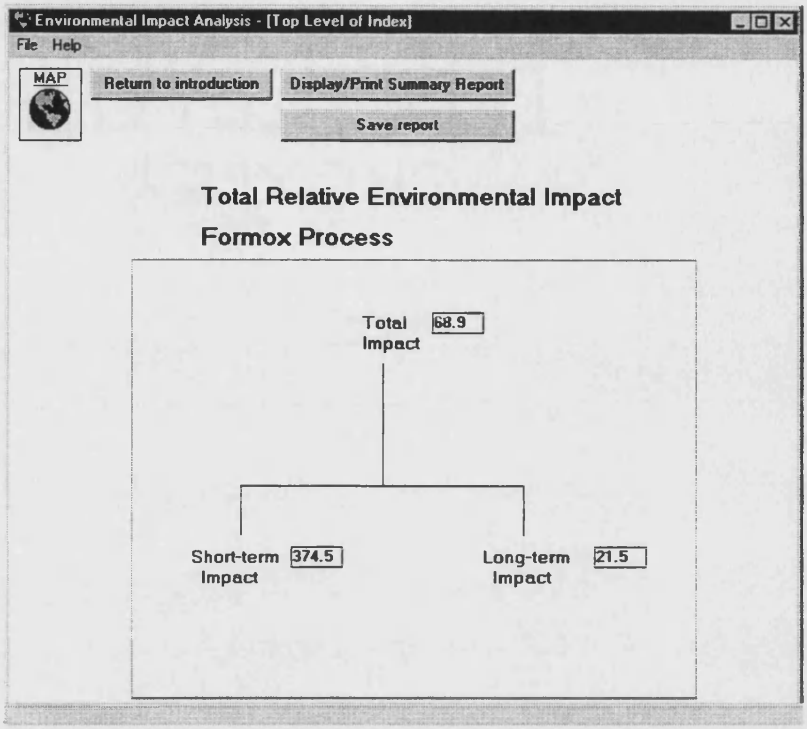

Figure 8.3 Levels 1 and 2 of EniVal for Formox process

The 'Map' icon in the top left corner of the screen shown in Figure 8.3 provides the user with a map of the current position in the overall tree structure of EniVal. The map as shown in Figure 8.4 is updated as the user follows the details of the analysis down through the tree structure.

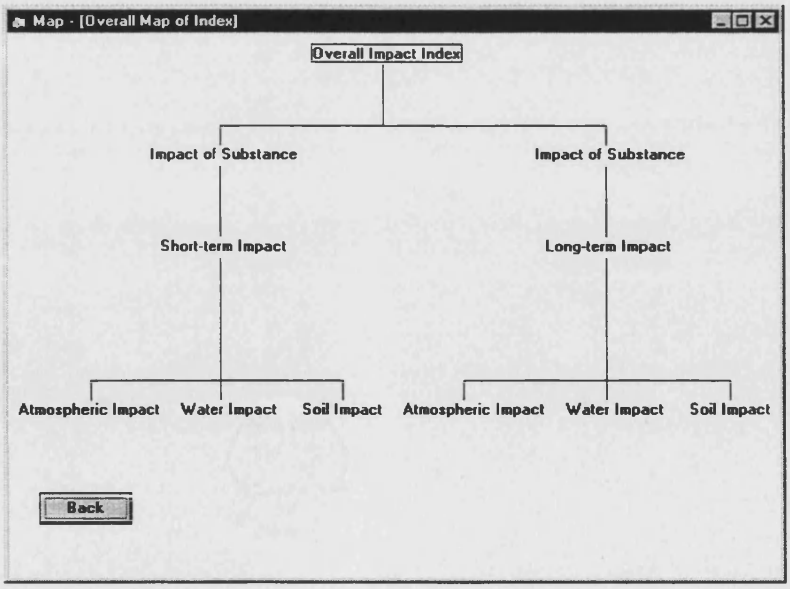

Figure 8.4 Map of EniVal structure

Sections 8.2 and 8.3 of this chapter describe the use of EniVal to analyse the relative environmental impacts of modifications to two continuous chemical processes. The first example investigates the effects of two process modifications on the relative environmental impact of the Formox process. The second example analyses two alternative designs for the nitrobenzene production process.

8.2 Formox process

As discussed in Chapter 6 the Formox process produces an aqueous solution of formaldehyde by the vapour phase oxidation of methanol over a fixed metallic catalyst bed. The simplified flowsheet for the process is presented again in Figure 8.5.

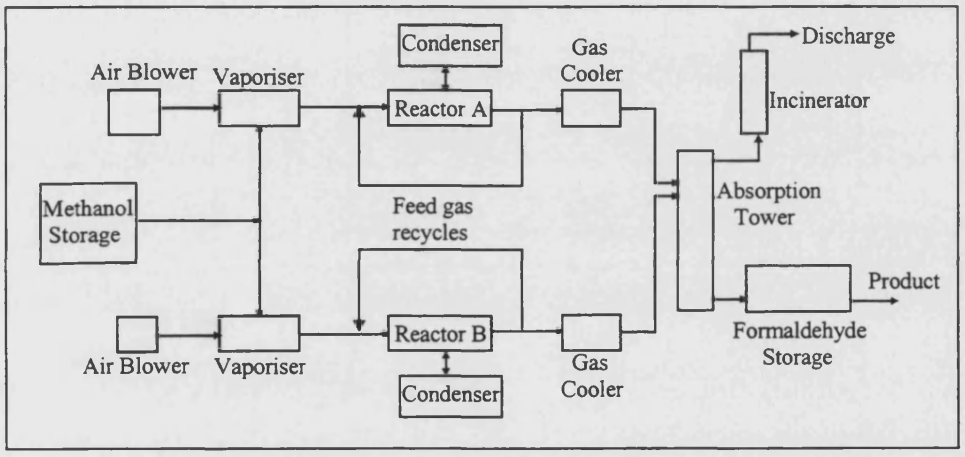

Figure 8.5 Formox process schematic diagram

The two main sources of pollution are the stack used to discharge the wastes from the incinerator and fugitive emissions from the tanks, pipelines and fittings. It is possible to reduce these emissions by changing the operation of the process. This section investigates the effects of minimising these emissions relative to the base case as presented in Table 8.1. The base case represents the operation of the process as described in Chapter 6 with no process modifications. When the base case was analysed using Option 3 in EniVal, an overall relative impact of 69 was calculated for the process as shown in Table 8.1.

Table 8.1 Formox process emission summary

Pollutant	Discharges (kg per annum)		
	Base Case	End-of-pipe treatment	Plant maintenance
Formaldehyde	11617	8795	5145
Methanol	13663	4632	11764
VOC (as Toluene)	7707	1542	7707
NO_2	257	257	257
Total Impact	69	33	51

Both of the pollution sources identified in Chapter 6 can be reduced through retrofitting the process. Firstly, the discharges from the incinerator can be significantly reduced by using end-of-pipe technology such as carbon adsorption to remove a given percentage of the organic pollutants. If it is assumed that 80% of the organic pollutants which are presently discharged through the stack can be removed using carbon adsorption then EniVal indicates that the total impact would drop by over 50% from 69 to 33. However this option would be quite expensive to install.

The alternative retrofit for the process would involve instigating a programme to monitor and repair any leaks from pipes and fittings on the plant. This can feasibly reduce the fugitive emissions by 80% and would be comparatively easy to set-up and maintain. In this case the overall impact would become 51 compared to the base case value of 69. While in this case the reduction in total impact is only 26%, it is probably the cheaper alternative. This simple case study shows that the end-of-pipe treatment for the incinerator stack is the more effective of the two alternatives for reducing the overall environmental impact of the process. However, further studies would have to be carried out to determine which of the alternatives was the more economically feasible. Only then could the Best Practicable Environmental Option (BPEO) be selected.

8.3 Nitrobenzene production

There are many different methods used to produce nitrobenzene including both batch and continuous processes. This investigation is concerned only with the continuously operated processes. The main variation which occurs between processes involves the nitration section of the plant. The traditional method of

production is to operate the nitration reactors isothermally and the nitrobenzene plant presented in Chapter 6 operates in this manner. Other operating options include adiabatic reaction, azeotropic distillation and nitration with concentrated nitric acid rather than the mixed acid which is more commonly used. Figure 8.6 which shows the schematic diagram for the process does not distinguish between the type of nitration reactors used within the process. From the alternative processes available for the nitration of benzene the isothermal and adiabatic processes were chosen for comparison.

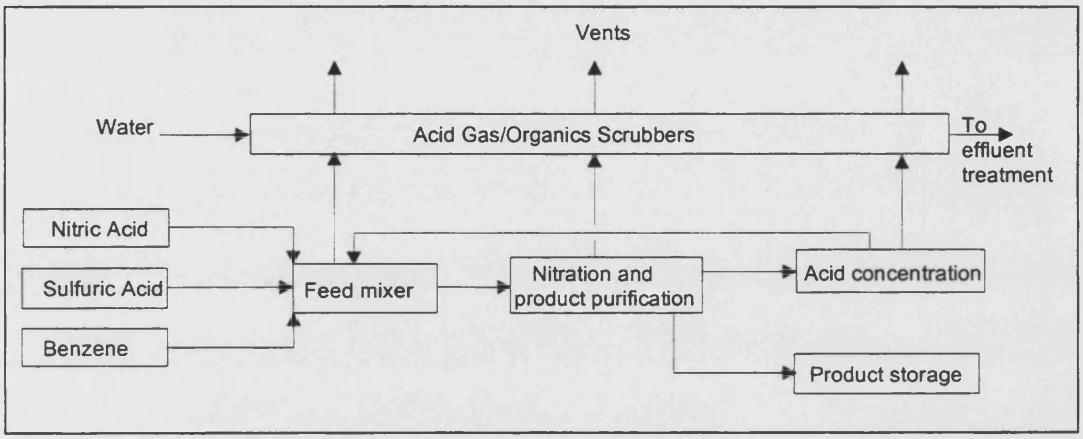

Figure 8.6 Nitrobenzene production schematic diagram

For the isothermal process as described in Chapter 6, EniVal returned a value of 843 for the total impact as shown in Table 8.2. As discussed in Chapter 7 the impact scores alone have little or no meaning. However the relative impact score for the isothermal case can be compared to that for the adiabatic process to see if the alteration to the reaction process makes a significant change to the overall impact of the process on the environment.

Table 8.2 Nitrobenzene process impact summary

	Discharges (tpa)	
Pollutant	Isothermal	Adiabatic
Water	11787	11787
Benzene	264	20
Sulphuric acid	24	1
Nitrobenzene	7	7
Sodium nitrate	287	22
Calcium sulphate	37660	1709
Iron sulphate	34	34
CO2	19261	19261
NOx	3	1
Total Impact	843	521

The adiabatic process has been reported to cost 30% less than the isothermal process and to require only about 10% of the energy needed for the traditional isothermal nitration techniques (Guenkel, Prime and Rae, 1981). The economic and energy savings must be compared to the environmental impact of the process relative to the isothermal process before a final reaction process can be selected.

The adiabatic process is purported to avoid the problems of sulphuric acid disposal and limit benzene emissions while at the same time providing yields of nitrobenzene greater than 99%. In the isothermal process the reaction temperature is maintained at 60°C by the use of cooling coils in the reactors. However in the adiabatic process the nitration occurs in a much greater volume of sulphuric acid than that used in the isothermal process. As the temperature in the reactor increases due to the exothermic nature of the reaction, the heat is absorbed by the large volume of sulphuric acid. The energy which is absorbed by the sulphuric acid results in a much lower energy requirement for the acid reconcentration which can now occur by flashing under vacuum. As the reaction proceeds through the nitrators, the temperature increases from 90°C to 135°C, which in turn increases the reaction rate. This increase in reaction rate compensates for the more dilute system created by the increased volume of sulphuric acid.

The reduced emissions shown in Table 8.2 were estimated from comparisons of the adiabatic with the isothermal processes (Guenkel, Prime and Rae, 1981). For these emissions the overall environmental impact was reduced to 521. This corresponds to a 38% reduction in overall impact compared to the isothermal process impact score of 843. Table 8.2 shows that the adiabatic process has considerably smaller releases of both benzene and sulphuric acid, both of which have relatively high impact scores. The operation of the nitrobenzene production process under adiabatic conditions allows for high conversion rates (which reduce the amount of unreacted benzene), and vacuum acid reconcentration (for which the sulphuric acid emissions are much lower) resulting in a much lower relative environmental impact score.

From the evidence presented here the adiabatic process is the better of the two options from the point of view of cost, energy and environmental impact. This would indicate that the adiabatic nitration process was the BPEO for the production of nitrobenzene.

8.4 Summary

This Chapter has described the implementation of EniVal as a computer-based tool which operates under the Windows environment. Section 8.1.1 discussed the reasons for the selection of Visual Basic™ as the development package including the simplicity of application development, the suitability of graphical user interfaces for inputting data and displaying impact results and the minimisation of required computing resources. The use of this graphical program was then presented in sections 8.2 and 8.3 for the Formox and nitrobenzene production processes respectively. These two case studies showed how EniVal can be used to select the minimum impact design alternatives for both retrofits and alternative process designs.

Chapters 3 to 8 have presented the full development of EniVal from a simple concept through to a complete, fully operational Windows-based computer program. Chapter 9 provides a summary of this development and discusses the possible improvements that could be made to EniVal in the future.

Chapter 9

Conclusions and future work

One of the major tasks of the Environment Agency in the UK is to provide an integrated approach to the protection of the environment based on the principles of Integrated Pollution Control (IPC). IPC was first introduced in the 1990 Environmental Protection Act (1990). The need for a tool which is capable of assessing the relative environmental impact of processes is integral to the implementation of the principles of BATNEEC and BPEO within the IPC legislation.

9.1 Conclusions

The potential environmental impact of a pollutant is a very difficult characteristic to assess because the point of reference changes depending on whether the assessment is being carried out for political or scientific reasons. Politically-based assessments are often used for regulation purposes to control the operation of existing processes. EniVal, the impact tool developed in this thesis, is based on a combination of both scientific and political priorities by incorporating specific information related to both the physical and chemical properties of the chemicals and the most current issues which are regarded as being of vital concern to the state of the environment. Typical examples of these issues include global warming, acid rain and the deoxygenation of the nation's rivers caused by the discharge of organic chemicals.

EniVal incorporates a series of scoring systems to provide scores for parameters which describe the impact of each pollutant on the environment. These scores are then combined to provide an overall impact score for each of those pollutants. The tree structure of EniVal is the basis for the calculations of both a long-term impact score and a short-term impact score for the atmosphere, the water and the soil systems. The parameter scores are combined using weighted sums where the weightings reflect the importance of each parameter in the overall measure of impact.

The overall parameter scores for each pollutant are then combined using data obtained from a set of fate and distribution models to provide an overall impact score for each pollutant on the whole environment. The fate and distribution models for the organic pollutants are based on equilibrium relations and an overall

environmental mass balance while the inorganic pollutants are characterised according to their solubility.

The impact scores which are defined using the parameters described above are combined with the discharge ratio for each pollutant to give a final impact score for that pollutant. The discharge ratio incorporates both the amount of the pollutant which is released and the production level of the process. In this way processes of varying production capacities can be compared.

EniVal calculates an impact score for each pollutant using the inverse logarithm to base 10 of the overall impact score for that pollutant, multiplied by the discharge quantity for that pollutant, divided by the production level of the process achieved for that discharge. Analyses of 12 continuous industrial processes indicates that this combination of impact scores and discharge data provided the best set of EniVal scores with respect to the range and spread of values, the errors involved in the calculation of the scores and the sensitivity of the scores to changes in the raw data.

The presentation of the analysis of environmental impact on a tree structure allows the information to be displayed in a manner which is understood easily. A tree structured system provides not only the overall impact score at the apex of the tree, but also a range of data and information at each level down through the analysis. This approach allows the user to identify those areas of the process which are causing the most significant damage to the environment. It also allows easy access to the raw data for all the parameters to show how the final impact values are calculated.

The most efficient and effective means of presenting the information contained within EniVal was to use the event-driven, visual programming package, Visual Basic™. The result was an independent, Windows™-based program which can run on a simple PC without the need for supporting software. The graphical, Windows™-oriented design of EniVal allows the user to move easily throughout the program and to view any stage of the analysis they wish.

Through the use of a computer-based system, EniVal combines the simplicity of tools such as the ELF and the chemical scoring systems discussed in Chapter 2, with the complexity of a multi-media, long-term and short-term analysis of the overall environmental impact of pollutants.

EniVal determines the total impact of a chemical using a combination of twenty-eight different parameters. The data for some of these parameters such as solubility and molecular weight are commonly available in literature and can be found for a wide variety of chemicals. Other parameters such as the bioconcentration factor, soil adsorption constant and half-lives are not as common and locating sufficient data may prove difficult for some chemicals. The list of property data provided in Appendix E shows that the data for some parameters had to be estimated for many of the chemicals as no literature sources could be found. EniVal requires data for all twenty-eight parameters for a full assessment of the potential environmental impact of any chemical. However at present it must be recognised that sufficient property data do not exist to fully assess all chemicals. In future these data should be made available to ensure a rigorous and comprehensive assessment of the impact on the environment of discharges from chemical processes. Standard data sheets for new chemicals such as those proposed under the Notification Of New Substances (NONS, 1994) regulations should include data for all the parameters identified in Chapter 4.

As identified in Chapter 1 the aims of this thesis were to develop and implement EniVal, a tool for assessing the relative environmental impact of continuous chemical processes. Previous attempts to assess environmental impact have floundered due to lack of data and the use of insufficient information to full describe the extent of the impact.

Unlike the quality indices discussed in Chapter 2 which assess the impact on individual media, EniVal is capable of assessing the total impact of a chemical processes on all three environmental media. By adopting this multi-media approach

EniVal also incorporates the long-term transport of pollutants both between and within the three environmental media.

Many impact assessment tools rely on environmental concentration data which are often only available through complex and sometimes uncertain environmental modelling. These tools, such as the Integrated Environmental Index developed by HMIP (1994b), are of limited use when the process is still in the preliminary design stage. EniVal uses the total mass of each pollutant discharged which can be determined relatively simply by performing a simple mass balance on the process or through on-line measurement. These data are generally more reliable and much easier to obtain.

Tools such as the Environmental Load Factor (Caughlin, 1993) only utilise discharge data to assess the environmental impact. No consideration is given to the varying impact that different chemicals have on the environment and the assumption is that each pollutant has a similar impact or load on the receiving environment. By incorporating both discharge data and a measure of the relative impact for each pollutant, the use of EniVal ensures that chemicals which may have small discharges but high impacts (such as heavy metals) contribute equally to the overall impact score.

EniVal produces reliable, consistent measures of environmental impact that are within an accuracy of ± 30% for chemical processes. These data when combined with preliminary process costing tools (which are of similar accuracy), can be used to determine the Best Practicable Environmental Option (BPEO) for a given process as shown in Chapter 8. The two case studies showed that EniVal is suitable for analysing alternative process designs as well as process retrofits. However, further modifications could be made to EniVal to improve its reliability and robustness as discussed in the following section and further testing on a wider range of processes is required.

9.2 Further enhancements of EniVal

The task of determining the total impact of a chemical process on the environment is an immense and very complicated undertaking. There are numerous issues which need to be considered, most of which will change along with our understanding of the effects of human processes on the environment. There is a range of modifications which could be made to EniVal in order to enhance its ability to best represent the impact of a process on the environment. These enhancements are discussed below.

EniVal could be modified to include an energy component to consider the 'energy costs' of environmental improvements. Many current environmental assessment techniques incorporate the principles of Life Cycle Analysis (LCA) whereby the full life of all materials involved in the process is considered in the analysis. Often the relative environmental impact of a process may decrease following the incorporation of cleanup technology which may be very energy intensive. The environmental impact caused by the production of this energy is not at present considered in the analysis of EniVal. An environmental energy cost factor could be introduced into EniVal as a separate component, similar to an extra pollutant at the top level of EniVal.

The two governing principles of clean process design as defined by HMIP are the Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and the Best Practicable Environmental Option (BPEO). The principles of BATNEEC and BPEO incorporate measures of both the economic cost and the environmental cost of the process. In its present form EniVal can only be used to determine the Best Environmental Option (BEO) and it must be used in conjunction with cost tools to determine the overall BPEO. A method of consistently comparing the environmental and economic costs of processes needs to be developed so that each analysis clearly presents one or two BPEO alternatives.

The long-term fate and distribution models incorporated in EniVal are relatively simple equilibrium models for three environmental media. For a more accurate analysis of the overall impact these models could be updated to analyse more than the

three basic media. Models can be developed for predicting the distribution of chemicals between water, air, soil, sediments, biota and other environmental media which would enhance the operation of EniVal. However for the purposes of the studies carried out in Chapter 8 the existing models are sufficient.

There are some chemicals which only exhibit certain detrimental effects when in the presence of other chemicals such as sodium metal in the presence of water. When isolated from all sources of water, sodium remains essentially non-reactive. However when brought into contact with water, a potentially explosive situation occurs and the sodium reacts very rapidly. In future a system whereby warning signs, or flags, could be built into EniVal for such incompatible chemicals to indicate to the user when unfavourable pairings arise. One possible way to identify these incompatible pairings is by using the table developed by Hatayama, Chen, de Vera, Stephens and Storm, (1980).

As discussed in Chapter 4 the parameters which are included in the modification branches of EniVal represent the current issues of most concern with regard to the state of the environment. As concerns for the environment change and new issues arise these modification parameters must be updated to ensure that the impact scores reflect the relevant political and scientific climates.

The weightings incorporated within EniVal to combine all the pollutant property and discharge data have been selected arbitrarily based on previous work and the developer's opinion. They can easily be changed within the computer-based EniVal and further work is required to validate the selection of an appropriate set of these weightings.

EniVal was designed for use as a tool to be used in the preliminary stages of the design process. The graphical Windows-based approach was adopted to provide the user with a simple system for determining environmental impact. The user is led through the analysis by the program while at the same time given enough freedom to interrupt or alter the analysis at any stage. All of the process data must be entered by

the user for each analysis, although they can rely on previously stored files of pollutant property data if required. One possible adaptation of EniVal would be to re-code the program in a procedural language such as FORTRAN or C for implementation within a larger process simulation and optimisation package. This would mean that the user could run a simple simulation of the process to identify all the emissions. This information could then be fed automatically to the environmental impact assessment code (currently EniVal) for determination of the relative overall environmental impact of the process design alternative.

At present EniVal incorporates minimal support for the user and no on-line help system. It was assumed that the user would be familiar with Windows programs and be able to navigate throughout the system without any special preliminary tutoring. A limited support system has been built into EniVal to provide the user with information on the range of data required for the pollutants. However a full Windows help system would ensure that the user would be able to operate EniVal without difficulty. Similarly a brief operating manual would also aid in the user's movement throughout the system.

Not all chemicals discharged from processes are those which are traditionally regarded as pollutants such as those presented in Chapter 5. In the production of foodstuffs, discharges are often composed of fats, oils and composite organic wastes for which the property data required by EniVal for all pollutants is often not available. For these processes, a simpler version of EniVal may be required which would utilise the limited range of property data which is available.

The analyses of the 12 processes presented in Chapter 6 involved the assessment of 32 different chemicals. The property data for all of these chemicals are stored in a data file ready for further use in future enquiries. This property data file needs to be expanded to incorporate all new pollutants which arise in future studies using EniVal.

With the modifications and improvements presented in section 9.2 the EniVal will be capable of assessing the relative environmental impact of any given chemical process on the environment. This will enable the reliable selection of the Best Practicable Environmental Option using the Best Available Techniques.

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Appendix A

'List of environmental quality indices'

Air Quality Indices						
Name	Variables	Equation	Range	Categories	Description	Reference
Green's Combined Index (CI)	SO_2, COH	$CI = 0.5\left(84SO_2^{0.431} + 26.6COH^{0.576}\right)$	0-100+	0-49 Desired level, clean, safe air 50-59 First alert, intermediate 60-69 Second alert 69+ Third alert 100+ Extreme level	Index is based on proposed and adopted air quality standards; SO_2 concs differ by a factor of 5.0; COH values differ by a factor of 3.33. Index is applicable only during colder seasons when SO_2 concs are elevated	1
Ontario Air Pollution Index (API)	SO_2, COH	$API = 0.2\left(30.5COH + 126.0SO_2\right)^{1.35}$	0-580+	0-31 Acceptable 32-49 Advisory level 50-74 First Alert 75-99 Second Alert 100+ Episode Threshold Level	The coefficients and exponent relate API values to pollution levels attained during past air pollution episodes	1
PINDEX	CO, SO_x TSP, NO_x, OX, HC	PINDEX = $\frac{TSP}{375} + \frac{SO_x}{1430} + \frac{NO_x}{514} + \frac{CO}{40000} + \frac{HC}{19300} + \frac{OX}{214} + SYN$ where SYN = PM-SO_x synergistic term	0-100+	N.A.	Actual pollutant concs. are divided by their respective tolerance factor (one-hour equivalent standard) which is based on the California or other appropriate standards. The OX value includes that estimated from $NO_x + HC + h\nu \Rightarrow OX$. The SYN term is the smallest of the PM or SO_x terms.	1

Name	Variables	Equation	Range	Categories	Description	Reference
Oak Ridge Air Quality Index (ORAQI)	CO, SO_x, TSP, OX, NO_2	ORAQI = $\left[5.7\sum_i\left(\frac{c_i}{S_i}\right)\right]^{1.37}$ c_i = conc. pollutant i s_i = std for pollutant i	0-1000	<20 Excellent 20-39 Good 40-59 Fair 60-79 Poor 80-99 Bad 100+ Dangerous	Index may be calculated for any combination of from i = 1 to 5 pollutants using nomograph; pollutant standards, S_i are 24 hr extrapolations of secondary NAAQS. When pollutant concs. are at background levels ORAQI = 10; when all concs. are at stds. ORAQI = 100.	1
Mitre Air Quality Index (MAQI)	CO, SO_2, TSP, OX, NO_2	$MAQI = \sqrt{\sum_i I_i^2}$ I_i = indicator for each pollutant i	0-3+	<1 no std exceeded 1 ≤ MAQI ≤ 3 stds met or exceeded > 3 one or more std exceeded	Index may be calculated for any combination of i = 1 to 5 pollutants; indicator I_i is based on secondary NAAQS: $I_i = \sqrt{\left[\left(\frac{Cia}{Sia}\right)^2 + \delta\sum_i\left(\frac{Cih}{Sih}\right)^2\right]}$ where c_{ia} = mean conc. of pollutant i, during longest measurement period a, as specified by std. s_{ia} c_{ih} = mean conc. of pollutant i, during hourly measurement period h, as specified by standard s_{ih} $\delta_i = 1$ if $(c_{ih})_i > s_{ih}$ $\delta_i = 0$ if $(c_{ih})_i < s_{ih}$	1

Name	Variables	Equation	Range	Categories	Description	Reference
Extreme Value Index (EVI)	CO, SO_2, TSP, OX	$EVI = \sqrt{\sum_i E_i^2}$ E_i = indicator for each pollutant i	0, >1	0 all stds being met >1 at least one std exceeded	Index may be calculated for any combination of i = 1 to 4 pollutants; E_i is based on those secondary NAAQS not to be exceeded more than once per year, e.g. the hourly stds and is given by $E_i = \sqrt{\sum_i \left(\frac{A_{ih}}{S_{ih}}\right)^2}$; $A_{ih} = \sum_j \delta(c_{ih})_j$ where A_{ih} = summation of those values c_{ih}, which exceed the hourly measurement period h, for pollutant i, as specified by std s_{ih} $\delta_i = 1$ if $(c_{ih})_i > s_{ih}$ $\delta_i = 0$ if $(c_{ih})_i < s_{ih}$	1
Combustion Product Index (CPI)	N.A.	$CPI = \frac{\text{Fuel Burned}}{\text{Ventilating Volume}}$	N.A.	N.A.	The fuel burned (tons) is obtained by inventorying fuel deliveries; ventilating volume (volume of air into which the fuel combustion products are mixed) is the product of the inventory area, mixing depth and wind speed	1

Name	Variables	Equation	Range	Categories	Description	Reference
Air Quality Index (AQI)	CO, SO_2, TSP, OX, NO_2	$AQI = \sum_i W_i \times Pl_i$ W_i = weighting factor for pollutant severity Pl_i = standardised pollutant index	N.A	N.A.	The AQI may be calculated for any combination of from i = 1 to 5 pollutants whose concentrations are predicted by a simple diffusion model using emission inventory data; the predicted concs. are then standardised to give the standardised pollutant index Pl_i: $Pl_i = \bar{Y} + \frac{S\left(X_i - \bar{X}_i\right)}{S_i}$ where: $\bar{Y}$ = preset mean S = preset std deviation s_i = std deviation of predicted pollutant concs. X_i = predicted pollutant conc. $\bar{X}_i$ = mean predicted pollutant conc.	1

Name	Variables	Equation	Range	Categories	Description	Reference
Primary Standards Index	CO, SO_2, TSP, OX, NO_x	$PSI = \sum_{i=1}^{n} 100 \times \frac{c_i}{c_{si}}$ where: c_i = conc. of pollutant i c_{si} = NAAQS of pollutant i	N.A.	N.A.	Based on NAAQS primary standards (1^o stds). The index is most often used as a maximum index i.e. the value of the index which is reported is the value for the pollutant which has the maximum PSI. Alternatively, all values of the PSI can be reported separately with an indication of what the value of each means.	1
Standardised Urban Air Quality Index (SUAQI)	CO, SO_2, TSP, OX, NO_x	**SUAQI** **Standard** 50 2^o NAAQS 100 1^o NAAQS 200 Alert 300 Warning 400 Emergency 500 Significant harm	0-500	0-49 Good 50-99 Satisfactory 100-199 Unhealthful 200-500 Hazardous	The SUAQI is a segmented linear function. From a plot of SUAQI against pollutant concentration, the relative index value can be read for a given pollutant concentration. The index is based on NAAQS and episode criteria.	1

Water Quality Indices					
Name	Variables	Equation	Range	Description	Reference
Arithmetic Water Quality Index (WQIA)	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3, PO_4, temperature deviation from equilibrium, turbidity, total solids, DO % saturation	$WQIA = \sum_{i}^{9} w_i T_i(p_i) = \sum_{i}^{9} w_i q_i$ p_i = measured value of the ith parameter T_i = quality rating transformation of the ith parameter value p_i into a quality rating q_i such that $T_i(p_i) = q_i$ w_i = relative weight such that $\sum_{i}^{9} \omega_i = 1$	96.3-7.5	This index was selected in the comparison to be the best and most accurate of the following 5 water quality indices. The highest value of the index indicates the highest quality and the lowest value indicates low quality. The same applies for all the indices except Harkin's where a low value of the index indicates high quality.	2
Multiplicative Water Quality Index (WQIM)	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3, PO_4, temperature deviation from equilibrium, turbidity, total solids, DO % saturation	$WQIM = \prod_{i=1}^{9} q_i^{w_i}$	N.A.	The same group of experts were used to determine the weightings. They were asked to rank the 11 parameters on a scale of 1 to 5 and the results were converted into weights by scaling the arithmetic means of each parameter's scores.	2

Name	Variables	Equation	Description	Reference
Harkin's Objective Water Quality Index	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3, PO_4, temperature deviation from equilibrium, turbidity, total solids, DO % saturation	$S_n = \sum_{1}^{p} \frac{(R_{in} - R_{ic})^2}{Var_i} \quad n = 1,2,\ldots q$ $Var_i = \left(\frac{1}{12q}\right)\left[q^3 - q - \sum_{j=1}^{k_i}(t_{ij}^3 - t_{ij})\right]$ S_n = Nth water sample in data set q = total number of water samples in the particular data set under consideration p = total number of parameters being used R_{in} = rank of the nth water sample, according to the value of the ith parameter, when compared to the values of that parameter among all of the q water samples R_{ic} = control value of the ith parameter Var_i = rank variance exhibited in the ordering of the ith parameter's values t_{ij} = number of elements involved in the jth tie encountered in ordering the values of the ith parameter	"Because the S_n values are a function of the rankings of the water samples for each parameter as well as the rank of the control value (which are a function of the specific values of the water samples in a particular set), the S_n values are not invariant over data sets. In other words a given water sample will take on different index values when it is considered within the context of different data sets. Hence S_n values must be recalculated every time a new comparison is to be made and that comparison is only valid for the data set over which S_n values were derived."	2

Name	Variables	Equation	Description	Reference
Unweighted Arithmetic Water Quality Index (WQIAU)	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3, PO_4, temperature deviation from equilibrium, turbidity, total solids, DO % saturation	$WQIAU = \left(\frac{1}{9}\right)\sum_{i=1}^{9} q_i$	The quality transformations were obtained from expert opinion. 70 persons with expertise in water quality management were asked to draw plots of quality against parameter value and the average curves were used for the transformations. (Brown et al.)	2
Unweighted Multiplicative Index (WQIMU)	Faecal coliform count, pH, biochemical oxygen demand (BOD), NO_3, PO_4, temperature deviation from equilibrium, turbidity, total solids, DO % saturation	$WQIMU = \left(\prod_{i=1}^{9} q_i\right)^{1/9}$	Similar to the WQIAU except multiplication not addition is used in to collate the quality ratings.	2

Other Environmental Quality Indices				
Name	Variables	Equation	Description	Reference
Pilot Environmental Quality Index for UK	NO_x emissions (thsd tonnes NO_2 equiv.), SO_2 urban concs. ($\mu g/m^3$), low-level O_3 concs. (average monthly 99th percentile), CO_2 emissions (million tonnes of carbon), Oil spills requiring clean-up (number), % length of river of poor or bad quality (percentage), resident population (millions), fertiliser deliveries to agricultural use (thsd tonnes), new dwellings started (thsds).	NO_x = 0.06 * Greenhouse effect + (Air pollution (local + national))/3 SO_2 = Air pollution (local + national)/3 O_3 = 0.12 * Greenhouse effect + (Air pollution (local + national))/3 CO_2 = 0.50 * Greenhouse effect Oil spills = Marine pollution Rivers = Pollution of rivers/lakes Population = (Access to countryside + loss of farmland + damage to landscape)/2 Fertilisers = Drinking water Dwellings = (Access to countryside + loss of farmland + damage to landscape)	The index is derived from the sum of the variables multiplied by their respective weightings which are derived from a combination of the data provided from the public opinion surveys. Public Opinion Categories: **Local**: Drinking water Noise Air pollution (local) Waste disposal Access to countryside Loss of farmland Damage to landscape **National**: Pollution of rivers and lakes Marine pollution Air pollution (national) Industrial waste disposal **Global**: Extinction of species Loss of natural resources Greenhouse effect	3

Name	Variables	Equation	Description	Reference
Environmental Load Factors (ELF)	All substances discharged from a site including the water in the aqueous discharges.	$ELF = \frac{\text{Total quantity discharged}}{\text{Total product produced}}$	The Environmental Load Factors are based on the total quantities of substances discharged to the environment. It is standardised against the quantity of product produced. It does not consider the different impacts that substances have on different environments. It also includes the water in the discharge which was introduced to the process but not the air.	4
HMIP Integrated Environmental Index (IEI)	All substances discharged from process	$IEI_{(process)} = \sum_{m=1}^{i} \sum_{s=1}^{i} \frac{\text{Plant contribution}_{s,m}}{EQS_{s,m} \text{ or } EAL_{s,m}}$ $EQ = \frac{\text{Plant contribution}}{\text{EQS or EAL}}$ (EQ - Environmental quotient) where: Plant contribution$_{s,m}$ = maximum long term average environmental conc. of substance s released to medium m. EQS = Environmental Quality Standard EAL = Environmental Assessment Level (Set by HMIP) when no EQS	The IEI assesses the environmental consequences of a process by examining the magnitude of release, ambient conc and the nature of the receiving environment for each pollutant. The relative hazard represented by various substances is accounted for by normalising the release in relation to an environmental quality criterion. The index is designed to be used in conjunction with other factors (MDR, GWP, POCP, Waste Hazard Potential)	5

Name	Variables	Equation	Description	Reference
Global Warming Potential (GWP)	CO_2, H_2O vapour, CH_4, nitrous oxide, CFCs (CFC 11, CFC 12, HCFC-22, HFC-134a)	$GWP_{Total} = \sum_{1}^{n} GWP_i \times Mass_i$ where: GWP_i = Global Warming Potential of substance i of n released from the process option $Mass_i$ = Mass of substance i of n released from process option	The global warming potential of each gas is the warming contribution of each gas relative to an equal weight of CO_2 over a period of 100 years.	5
Photochemical Ozone Creation Potential (POCP)	Volatile Organic Compounds, NO_x	$POCP_{Total} = \sum_{1}^{n} POCP_i \times Mass_i$ where: $POCP_i$ = the POCP for substance i of n substances released from the process. $Mass_i$ = annual mass of substance i released from the process	The change in photochemical ozone production due to a change in emission of particular VOCs. Data is provided as to the individual average POCPs for groups of relevant VOCs.	5
Waste Hazard Potential	Solid or liquid wastes which are not released to air or water e.g. Cd, Ni, Vinyl Chloride, Benzene, Hg, Acrylo-nitrile, Formaldehyde, Cr, Dichloro-methane, Ethyl benzene, 1,3 Butadiene, Methyl ethyl ketone, Styrene, Xylene, Toluene.	Final Hazard Score = $\text{Log}_{10}(\text{Quantity for disposal}_i) \times$ Unit Hazard Score	Each waste produced is assessed quantity and relative hazard potential. The relative hazard potential is determined by its physical, chemical and biological characteristics. These include: (i) toxicity (mammals & aquatic species) (ii) potential for bioaccumulation (iii) degradation (in soil/water); and (iv) other physical characteristics such as solubility, adsorption potential.	5

Name	Variables	Equation	Description	Reference
Maximum Deposition Rate (MDR)	Pollutants discharged to soil	$MDR = \frac{(SQC - AMB_s) \times D_s \times d_s}{T}$ where: MDR = provisional maximum deposition rate ($mg/m^2/day$) SQC = selected soil quality criteria (mg/kg dry soil) AMB_S = median soil pollutant conc. D_S = soil density ($1000\ kg/m^3$) d_S = mixing depth for pollutant concerned (7.5 cm)	The maximum deposition rate is the quantity of pollutant which can be added to the solid daily over a 100 year period before the selected soil quality criterion is exceeded. The soil quality criterion is corrected for the median ambient soil pollutant conc. No allowance has been made for degradation or other removal processes in the soil. Thus it will underestimate the values for some readily degradable substances.	5

Name	Variables	Equation	Description	Reference
Shanks & McEwan	Wastes which are considered to have hazardous properties (H1-H14) if they contain any of the hazardous constituents listed in **Annex II of EC Directive 91/689/EEC**	$\frac{100}{QH} \times \left[QH - \left(Qh_{BAD(air)} + Qh_{BADwater)} + Qh_{BAD(land)} \right) - \left(\frac{Qh_{D(air)}}{t_{1(air)}} + \frac{Qh_{D(water)}}{t_{2(water)}} + \frac{Qh_{D(land)}}{t_{3(land)}} \right) \right]$ where: QH = units of quantity of the hazardous constituents (C1-C51) which are contained within the waste product. Qh_D = Unit of quantity of hazard constituents (C1-C51) discharged over time to air water and land during the use of the waste disposal technique considered. This excludes discharges which are bio-accumulative or ozone-depleting. These discharges are accounted for under Qh_{BAD} Qh_{BAD} = Units of quantity of hazardous constituents which are bio-accumulative and are discharged to air water and land during the use of the waste disposal technique under consideration. t_1, t_2, t_3 = time over which the discharges to the unmanaged environmental media of air, water or land take place. For joint disposal to land, the time period begins after the waste has left any container and is in contact with the putrescible medium. Wastes which continue discharges after more than 2 years are considered unsuitable for land disposal.	The formula measures both the quantity of hazardous constituents as an input to the disposal technique, and the quantity of hazardous constituents discharged. The relative weightings for those discharges which are either bio-accumulative or damaging to upper atmosphere ozone are increased by not dividing them by the period of time over which the discharge takes place. The formula is inadequate in that it allows the movement of wastes from one medium to another where the chemical is not considered to be a pollutant e.g. CO_2 in the atmosphere favours incineration as the disposal technique.	6

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Appendix B

'Development of preliminary pollutant distribution model'

Model 1

The first attempt made to develop a suitable model was based on comparing the probabilities that chemicals would move from one medium to another. This movement was described using several parameters which were functions of the chemical's physical and chemical properties. For the air-water system, the chosen parameter was the Henry's Law constant H, or the Air-Water Partition coefficient K_W (inverse of H). For the soil-water system, the soil adsorption coefficient K_{OC}, was used to provide an estimate of the distribution. There was no single parameter which could be used to describe the equilibrium distribution of a chemical between the soil and the air. This was mainly due to the fact that there were several pathways by which the chemical could move between the soil and the air. The movement along these pathways is often a function of the amount of air and water within the soil. In order to deal with this problem, two parameters were developed to describe the interactions in the soil-air system. They were functions of both K_W and K_{OC} according to whether the transport was via the soil air or the soil water. This was dictated by the values of K_W.

In order to provide a useful analysis of the distribution, the parameters had to be scaled so that they were all considered over the same range. It was decided to scale them between the values of 0 and 1 according to a maximum and a minimum value by the following equation.

$$P_{Scaled} = \frac{P - P_{Min}}{P_{Max} - P_{Min}} \quad ; \quad 0 \le P_{Scaled} \le 1 \qquad \text{(B-1)}$$

where P is the parameter in question.

Laskowski had developed an expression for the potential soil volatility for dry soil which was related to the percentage of the pollutant in the soil air. This was given by the following equation.

$$\% \text{ in soil air} = \frac{100x}{x + yK_w + zdf_{oc}K_wK_{oc}} \qquad \text{(B-2)}$$

where x, y, z are the fractions of air, water and solids respectively;

d is the soil density; and

f_{OC} is the fraction of organic carbon in the soil.

From this, an expression was obtained for the ratio of the amount of chemical in the soil air (an indication of the amount transferred to the atmosphere) to the amount in the soil itself. This was given by:

$$\frac{\text{Amt(Air)}}{\text{Amt(Soil)}} = \frac{x}{yK_w + zdf_{oc}K_wK_{oc}} \qquad \text{(B-3)}$$

The transport was considered to be dry if the K_W of the chemicals was less than 10,000, and wet if the K_W was greater than 30,000 (?Ref). In between these values there was a transition period. For wet transport the distribution was governed by the equation:

$$\frac{\text{Amt(Air)}}{\text{Amt(Soil)}} = \frac{1}{K_wK_{oc}} \qquad \text{(B-4)}$$

Thus the final distribution for the soil-air system was governed by the following set of equations:

$$\frac{\text{Amt(Air)}}{\text{Amt(Soil)}} = \frac{x}{yK_w + zdf_{oc}K_wK_{oc}} \quad ; \quad K_w \leq 10{,}000 \qquad \text{(B-5)}$$

$$\frac{Amt(Air)}{Amt(Soil)} = \frac{x(1-a)}{yK_w + zdf_{oc}K_wK_{oc}} + \frac{a}{K_wK_{oc}} \quad ; \quad 30000 \rangle K_w \rangle 10000 \qquad \textbf{(B-6)}$$

$$\frac{Amt(Air)}{Amt(Soil)} = \frac{1}{K_wK_{oc}} \quad ; \quad K_w \geq 30{,}000 \qquad \textbf{(B-7)}$$

Thus all three systems were fully defined using these equations and the values of K_W and K_{OC}. However the next problem was that maximum and minimum values had to be defined for each of the systems in order to scale the parameters. The problem became extremely complex when it came to defining these limits for the single parameters K_W and K_{OC}, and appeared even more complex for the soil-air system. After extensive research it was decided to abandon this model and consider a different approach which would not involve this problem of limits.

Appendix C

'Volume fractions for long-term fate and distribution model'

Air System

The atmosphere is split into 4 main layers
Only two are worth considering for environmental impact

Troposphere	The earth's weather conditions are limited to this layer which is relatively thin, extending upwards to about 8 kms at the poles and 15 km at the equator. It contains about 85% of the total atmospheric mass and almost all the water vapour.
Stratosphere	A thin layer of ozone contained within the stratosphere absorbs ultra-violet light and in the process gives off heat. This layer is included solely because of effects on this ozone layer.

Assume that earth is approximately spherical

Average diameter =	12742	km
Take height as	53	km
Volume of earth =	1.1×10^{12}	km^3
Volume of earth & atm =	1.1×10^{12}	km^3
Volume of atmosphere =	2.7×10^{10}	km^3
=	2.7×10^{19}	m3

Water System

Average depth of oceans and seas = 3808 m

Total volume of oceans and seas 1.3×10^{18} m3

Oceans and Seas are 97% of all water

Total water = 1.4×10^{18} m3

Fresh water = 4.1×10^{16} m3

75% of fresh water is land ice

Land ice = 3.1×10^{16} m3

Soil water is 0.025% of fresh water

Soil water = 1.0×10^{13} m3

For the remainder of fresh water

Rivers and lakes = 1.1×10^{16} m3

Total water system considered

Volume = 1.4×10^{18} m3

Water Body	Area km2
Pacific Ocean	165721000
Atlantic Ocean	81660000
Indian Ocean	73442000
Arctic Ocean	14351000
Mediterranean Sea	2966000
Bering Sea	2274000
Caribbean Sea	1942000
Gulf of Mexico	1813000
Sea of Okhotsk	1528000
East China Sea	1248000
Hudson Bay	1230000
Sea of Japan	1049000
North Sea	575000
Black Sea	448000
Red Sea	446000
Baltic Sea	423000
Persian Gulf	238000
Gulf of St Lawrence	236000
English Channel and Irish Sea	179000
Gulf of California	161000
Total	351930000

Soil System

Soil has 4 horizons below the surface A, B, C, and the underlying consolidated rock R

Below a depth of 1 m the soil is clayey, impermeable and a serious impediment to plant growth.

Take as the soil depth which needs to be considered as

Average soil depth considered =	1	m
Fraction of land on earth =	30%	
Fraction of land covered in soil =	60%	
Fraction of earth covered by soil =	18%	
Average diameter of earth =	12742	km
Volume of earth =	1.1×10^{12}	km3
Volume of earth and soil =	1.1×10^{12}	km3
Volume of soil considered =	9.2E+04	km3
=	9.2×10^{13}	m3

Appendix D

'Results from long-term fate and distribution model'

Chemical	Kw	$Koc \times \rho_s \times f_{oc}$	Fa	Fw	Fs
1,2 Dichloroethane	25.03	3432.00	0.40	0.49	0.11
1,4 Dioxane	5011.04	1766.17	0.00	0.89	0.11
111 Trichloroethane	3.06	19032.00	0.74	0.11	0.15
2 Nitropropane	198.81	603.20	0.09	0.88	0.04
Acetic Acid	244538.80	84.70	0.00	0.99	0.01
Acetone	666.32	1.44	0.03	0.97	0.00
Benzene	4.49	10192.00	0.73	0.16	0.11
Butanol	4390.28	7488.00	0.00	0.66	0.34
CCl4	0.80	11440.00	0.93	0.04	0.03
Carbon Disulphide	17.47	6552.00	0.44	0.38	0.17
Chloroform	5.62	3536.00	0.74	0.21	0.05
Cyclohexane	0.13	49920.00	0.97	0.01	0.02
Dichloromethane	9.12	2479.50	0.65	0.30	0.05
Diethylamine	951.51	5200.00	0.02	0.73	0.26
Dimethylamine	1381.58	1560.00	0.01	0.89	0.09
Ethanol	3887.74	1.44	0.01	0.99	0.00
Ethanolamine	611347.00	520.00	0.00	0.97	0.03
Ethyl Acetate	203.78	1031.89	0.08	0.86	0.06
Ethyl Chloride	2.88	3432.00	0.85	0.12	0.03
Ethyl Formate	63.52	3328.00	0.21	0.65	0.15
Ethylene Glycol	407564.67	1.44	0.00	1.00	0.00
Ethylamine	1988.12	1.44	0.01	0.99	0.00
Freon 11	0.25	9742.05	0.98	0.01	0.01
Freon 112	0.25	32656.00	0.96	0.01	0.03
Freon 113	0.05	19864.00	0.99	0.00	0.00
Freon 114	0.01	31200.00	1.00	0.00	0.00
Furan	4.53	2808.00	0.79	0.18	0.03
Isoamyl Acetate	41.66	6864.00	0.25	0.51	0.24
Isopropanol	3030.22	1.44	0.01	0.99	0.00
MIBK	260.15	1976.00	0.06	0.83	0.11
Methanol	181.14	1.44	0.10	0.90	0.00
Methyl Ethyl Ketone	2328.94	3536.00	0.01	0.80	0.19
Methylamine	2203.05	1248.00	0.01	0.91	0.08
Morpholine	173431.77	832.00	0.00	0.95	0.05
Piperidine	5495.25	1.44	0.00	1.00	0.00
Pyridine	3.49	1.44	0.85	0.15	0.00
Tetrachloroethylene	1.64	21840.00	0.83	0.07	0.10
Tetrahydrofuran	2.54	1.44	0.89	0.11	0.00
Toluene	4.12	10400.00	0.74	0.15	0.11
Tributylamine	13.36	59280.00	0.23	0.15	0.62
Trichloroethylene	2.37	10400.00	0.83	0.10	0.07
Triethylamine	177.20	1144.00	0.10	0.84	0.07
m-Xylene	3.18	17264.00	0.74	0.12	0.14
p-Xylene	3.18	21216.00	0.72	0.11	0.16

Koc - mg/g / mg/l Kw - []

Appendix E

'Physical and chemical property data for EniVal'

		Zinc		Nitric acid		Sulphur dioxide		Calcium sulphate	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number		7440-66-6		7697-37-2		7446-09-5		7778-18-9	
OEL	mg/m3	10 (TLV)	1	5	6	5	6	10000	1
EC50 (microtox)		N.A.		N.A.		N.A.		N.A.	
Carcinogenicity	-	2 (Class D)	2	0	1	10	1	0	1
Reprod. test conc.		N.A.		0	1	N.A.		N.A.	
Potential for metabolites	-	8	*	0	*	5	1	1	1
log(Kow)	-	3	?	0	?	1.8	?	0	?
Pollutant type	-	1	*	5	*	3	*	6	*
Material Factor	-	1	3	0	1	1	3	0	?
Explosive decomposition	-	2	1	0	1	3	1	0	1
Detonation	-	0	1	0	1	0	1	0	1
Solubility	ppb	0	4	∞	4	10000000	4	3000000	1
Vapour Pressure	kPa	0	4	0	4	101	4	0	?
Bioconcentration factor	-	1000	?	0	?	0	?	0	1
Boiling point	°C	907	4	86	4	-10	4	1200	1
Half-life (a)	s	years	1	years	1	months	?	days	?
Half-life (w)	s	years	1	years	1	months	?	days	?
Half-life (s)	s	years	1	years	1	months	?	days	?
Acid Rain	-	0	*	10	*	10	*	0	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	0	5	0	5	0	5	0	5
UOD	-	0	*	4.57	*	0	*	0	*
Aesthetics (a)	-	0	1	0	1	0	1	0	1
Aesthetics (w)	-	0	1	0	1	0	1	0	1
Aesthetics (s)	-	4	1	0	1	0	1	1	1
Molecular weight	g/mole	65.38	1	63	4	64.06	4	145.15	1
Henry's Law constant	atm m3/mol	-	-	-	-		-		-
Soil Adsorption constant	mg/g/mg/l	-	-	-	-		-		-
Land reusability	-	10	8	4	8	0	8	0	8

		Sodium nitrate		Cadmium		Copper		Nickel	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number		07631-99-4		7440-43-9		7440-50-8			
OEL	mg/m3	1000 (LC50)	1	0.05	6	1	6	0.5	6
EC50 (microtox)		N.A.		N.A.		N.A.		N.A.	
Carcinogenicity	-	0	1	8	2	2 (Class D)	2	10 (Class A)	2
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	1	1	8	*	4	1	8	1
log(Kow)	-	0	?	3	?	2	?	3	1
Pollutant type	-	6	*	1	*	1	*	1	*
Material Factor	-	0	?	0	1	0	1	55	1
Explosive decomposition	-	1	1	0	1	0	1	0	1
Detonation	-	0	1	0	1	0	1	0	1
Solubility	ppb	10000000	4	0	4	0	4	0	4
Vapour Pressure	kPa	0	?	0	4	0	4	0	4
Bioconcentration factor	-	0	1	1000	?	10	?	10	1
Boiling point	°C	380	1	767	4	2300	4	2900	4
Half-life (a)	s	weeks	?	years	?	years	?	200 days	1
Half-life (w)	s	weeks	?	years	?	years	?	200 days	1
Half-life (s)	s	weeks	?	years	?	years	?	200 days	1
Acid Rain	-	0	*	0	*	0	*	0	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	0	5	0	5	0	5	0	5
UOD	-	4.57	*	0	*	0	*	0	*
Aesthetics (a)	-	0	1	0	1	0	1	0	1
Aesthetics (w)	-	0	1	0	1	0	1	0	1
Aesthetics (s)	-	0	1	2	1	2	1	2	1
Molecular weight	g/mole	85	1	112.41	4	63.6	4	58.69	4
Henry's Law constant	atm m3/mol	-	-	-	-	-	-	-	-
Soil Adsorption constant	mg/g/mg/l	-	-	-	-	-	-	-	-
Land reusability	-	0	8	10	8	5	8	10	8

		Lead		Particulates		Xylenes		Pentane	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number						1330-20-7		109-66-0	
OEL	mg/m3	0.15	6	1	*	435	6	1800	6
EC50 (microtox)		N.A.		N.A.		16.1	7	N.A.	
Carcinogenicity	-	7	2	1000	*	2 (Class D)	2	10	2
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	8	1	2	*	2	1	1	1
log(Kow)	-	3	1	0	*	3.15	10	0	?
Pollutant type	-	1	*		*	0	*	0	*
Material Factor	-	2	1	0	*	16	3	21	3
Explosive decomposition	-	0	1	0	*	0	1	0	1
Detonation	-	0	1	0	*	3	1	2	1
Solubility	ppb	0	4	0	*	156000	10	200000	4
Vapour Pressure	kPa	0	4	0	*	1.2	10	101	4
Bioconcentration factor	-	1000	1	0	*	3	10	0	?
Boiling point	°C	1620	1	N.A.		140	10	-42.2	4
Half-life (a)	s	200 days	1	years	*	20 hours	10	weeks	1
Half-life (w)	s	200 days	1	years	*	3 days	10	weeks	1
Half-life (s)	s	200 days	1	years	*	1 week	10	weeks	1
Acid Rain	-	0	*	0	*	10	*	10	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	0	5	0	5	81	5	37	5
UOD	-	0	*	26	*	21.36	*	13.35	*
Aesthetics (a)	-	0	1	8	*	1	1	0	1
Aesthetics (w)	-	0	1	0	*	0	1	0	1
Aesthetics (s)	-	5	1	2	*	0	1	0	1
Molecular weight	g/mole	207.21	1	200	*	106.2	10	44.1	4
Henry's Law constant	atm m3/mol	-	-	-	-	0.00768	10	1	*
Soil Adsorption constant	mg/g/mg/l	-	-	-	-	3	10	5	*
Land reusability	-	10	8	0	8	0	8	0	8

		Chromium		Iron sulfate		Sodium hydroxide		Aluminium chloride	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number		7440-47-3							
OEL	mg/m3	0.05	6	1	6	2 (TLV)	1	2	6
EC50 (microtox)		N.A.		N.A.		N.A		N.A.	
Carcinogenicity	-	10 (Class A)	2	0	1	0	1	0	1
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	8	1	5	1	0	1	3	1
log(Kow)	-	3	?	0	?	0	?	0	?
Pollutant type	-	1	*	2	*	6	*	2	*
Material Factor	-	0	1	0	1	0	1	0	?
Explosive decomposition	-	0	1	0	1	0	1	0	1
Detonation	-	0	1	0	1	0	1	0	1
Solubility	ppb	0	4	480000000	1	1090000000	4	700000000	4
Vapour Pressure	kPa	0	4	0	?	0.4	1	0	1
Bioconcentration factor	-	1000	?	0	1	0	1	0	?
Boiling point	°C	2200	4	300	1	142	1	180	4
Half-life (a)		years	?	5 days	1	5 days	1	weeks	?
Half-life (w)		years	?	5 days	1	5 days	1	weeks	?
Half-life (s)		years	?	5 days	1	5 days	1	weeks	?
Acid Rain	-	0	*	0	*	0	*	0	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	0	5	0	5	0	5	0	5
UOD	-	0	*	0	*	0	*	0	*
Aesthetics (a)	-	0	1	0	1	0	1	0	1
Aesthetics (w)	-	0	1	0	1	3	1	5	1
Aesthetics (s)	-	2	1	5	1	0	1	5	1
Molecular weight	g/mole	52.01	1	152	1	40	1	133.34	4
Henry's Law constant	atm m3/mol	-	-	-	-	-	-	-	-
Soil Adsorption constant	mg/g/mg/l	-	-	-	-	-	-	-	-
Land reusability	-	10	8	0	8	0	8	0	8

		Carbon dioxide		Formaldehyde		Methanol		Toluene	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number		124-38-9							
OEL	mg/m3	9000	6	16	6	260	6	188	6
EC50 (microtox)		N.A.		9000	7	40340	7	49000	7
Carcinogenicity	-	0	1	2	1	0	1	0	1
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	0	1	3	1	5	1	3	1
log(Kow)	-	0	?	0.35	9	-0.77	10	2.73	10
Pollutant type	-	3	*	0	*	0	*	0	*
Material Factor	-	0	1	5	3	12	3	15	3
Explosive decomposition	-	0	1	3	1	2	1	2	1
Detonation	-	0	1	0	1	0	1	3	1
Solubility	ppb	1600000	4	∞	9	∞	10	543800	10
Vapour Pressure	kPa	101	4	518	9	12.3	10	3.8	10
Bioconcentration factor	-	0	1	0	9	2	10	98	10
Boiling point	°C	-78.5	4	-19.5	9	64.7	10	110.6	10
Half-life (a)	s	years	?	86400	11	259200	11	36000	11
Half-life (w)	s	years	?	86400	11	86400	11	345600	11
Half-life (s)	s	years	?	86400	11	86400	11	345600	11
Acid Rain	-	0	*	10	*	10	*	10	*
GWP	-	1	5	0	5	0	5	0	5
POCP	-	0	5	57	5	12	5	81	5
UOD	-	0	*	2.67	*	2.67	*	18.7	*
Aesthetics (a)	-	2	1	5	1	5	1	5	1
Aesthetics (w)	-	0	1	0	1	0	1	0	1
Aesthetics (s)	-	0	1	0	1	0	1	0	1
Molecular weight	g/mole	44	1	30.03	9	32.04	10	92.13	10
Henry's Law constant	atm m3/mol	-	-	3.27E-07	9	0.000135	10	0.00594	10
Soil Adsorption constant	mg/g/mg/l	-	-	0.01	9	0.01	10	100	10
Land reusability	-	0	8	0	8	0	8	0	8

		Nitrogen oxides		Hydrogen		Mercury		Water	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number									
OEL	mg/m3	5	6	1000	?	0.05	6	0	*
EC50 (microtox)		N.A.		N.A.		N.A.		N.A.	
Carcinogenicity	-	0	1	0	1	0	1	0	*
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	5	1	0	1	3	1	0	1
log(Kow)	-	0	?	0	?	2.5	?	0	?
Pollutant type	-	3	*	3	*	1	*	5	*
Material Factor	-	16	3	21	3	0	?	0	*
Explosive decomposition	-	0	1	5	1	0	1	0	1
Detonation	-	0	1	5	1	0	1	0	1
Solubility	ppb	∞	*	0	?	0	4	∞	*
Vapour Pressure	kPa	101	*	101	*	0	1	5	?
Bioconcentration factor	-	0	?	0	12	1000	?	0	?
Boiling point	°C	21	1	-253	12	356.9	4	100	*
Half-life (a)	s	days	?	years	?	years	?	years	*
Half-life (w)	s	days	?	years	?	years	?	years	*
Half-life (s)	s	days	?	years	?	years	?	years	*
Acid Rain	-	10	*	0	*	0	*	0	*
GWP	-	10	5	0	5	0	5	0	5
POCP	-	27	5	0	5	0	5	0	5
UOD	-	0	*	0	*	0	*	0	*
Aesthetics (a)	-	5	1	0	1	0	1	2	*
Aesthetics (w)	-	0	1	0	1	0	1	0	*
Aesthetics (s)	-	0	1	0	1	0	1	0	*
Molecular weight	g/mole	46.01	1	2	9	200.61	4	18	*
Henry's Law constant	atm m3/mol	-	-	-	-	-	-	-	-
Soil Adsorption constant	mg/g/mg/l	-	-	-	-	-	-	-	-
Land reusability	-	0	8	0	8	10	8	0	8

		Ethane		Nitrobenzene		Benzene		Sulfuric acid	
		Data	Source	Data	Source	Data	Source	Data	Source
CAS Number				98-95-3				7664-93-9	
OEL	mg/m3	5000	?	5	6	16	6	1000 (TLV)	1
EC50 (microtox)		N.A.		30	7	75	7	N.A.	
Carcinogenicity	-	0	1	0	1	10	1	0	1
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	2	1	4	1	3	1	7	1
log(Kow)	-	1.78	*	1.85	9	2.13	10	0	?
Pollutant type	-	0	*	0	*	0	*	5	*
Material Factor	-	21	1	24	3	16	3	0	?
Explosive decomposition	-	0	1	0	1	0	1	5	1
Detonation	-	4	1	3	1	0	1	0	1
Solubility	ppb	0	4	1900000	9	1791000	10	∞	*
Vapour Pressure	kPa	101	*	0.02	9	12.7	10	0	1
Bioconcentration factor	-	6.5	*	25	9	4	10	0	?
Boiling point	°C	-88.6	4	210.8	9	80.1	10	327	1
Half-life (a)	s	hours	?	0.544 hours	11	2.1 days	11	days	?
Half-life (w)	s	days	?	13.4 days	11	5 days	11	days	?
Half-life (s)	s	days	?	13.4 days	11	5 days	11	days	?
Acid Rain	-	5	*	10	*	10	*	10	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	8	5	81	5	19	5	0	5
UOD	-	5.34	*	20.59	*	16.02	*	0	*
Aesthetics (a)	-	0	1	4	1	0	1	0	1
Aesthetics (w)	-	0	1	6	1	0	1	0	1
Aesthetics (s)	-	0	1	1	1	0	1	0	1
Molecular weight	g/mole	30.07	4	123.11	9	78.11	10	98.08	1
Henry's Law constant	atm m3/mol	1	*	2.44E-05	9	0.00543	10	-	-
Soil Adsorption constant	mg/g/mg/l	222	*	56	9	98	10	-	-
Land reusability	-	0	8	0	8	0	8	0	8

		Ethyl chloride		Ethylene		Chlorine		Hydrogen chloride	
CAS Number		Data	Source	Data	Source	Data	Source	Data	Source
OEL	mg/m3	2600	6	5000	?	1.5	6	7	6
EC50 (microtox)		1000	12	N.A.		N.A.		282	12
Carcinogenicity	-	1	12	0	?	0	1	0	1
Reprod. test conc.		N.A.		N.A.		N.A.		N.A.	
Potential for metabolites	-	2	1	0	*	7	1	4	1
log(Kow)	-	1.43	10	0.77	*	0	?	0	?
Pollutant type	-	0	*	0	*	3	*	3	*
Material Factor	-	18	3	24	3	16	3	0	?
Explosive decomposition	-	2	1	3	1	3	1	0	1
Detonation	-	3	1	0	1	0	1	0	1
Solubility	ppb	5710000	10	150000000	4	1700000000	4	823000000	12
Vapour Pressure	kPa	101	10	101	4	707	4	15600	12
Bioconcentration factor	-	6.3	10	0.9	1	0	?	0	?
Boiling point	°C	12.3	10	-103.9	4	-34.6	4	-85	12
Half-life (a)	s	6.67 days	11	6.2 hours	11	hours	?	days	?
Half-life (w)	s	7 days	11	1 day	11	days	?	days	?
Half-life (s)	s	7 days	11	1 day	11	days	?	days	?
Acid Rain	-	5	*	5	*	0	*	0	*
GWP	-	0	5	0	5	0	5	0	5
POCP	-	2	5	91	5	0	5	2	5
UOD	-	5.34	*	5.34	*	0	*	0	*
Aesthetics (a)	-	0	1	0	1	5	1	0	1
Aesthetics (w)	-	0	1	0	1	0	1	0	1
Aesthetics (s)	-	0	1	0	1	0	1	0	1
Molecular weight	g/mole	64.52	10	28.05	4	70.91	4	36.47	4
Henry's Law constant	atm m3/mol	0.00848	10	5E-09	*	-	-	-	-
Soil Adsorption constant	mg/g/mg/l	33	10	63	*	-	-	-	-
Land reusability	-	0	8	0	8	0	8	5	8

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* These values were estimated from common correlations or were based on other similar properties

? These values are not available in literature and have been estimated using knowledge of similar chemicals.

Appendix F

'Error analysis for the calculation of impact scores'

Error Calculations

The maximum error which will occur in the estimation of the impact scores for any given chemical has been estimated using the tables on pages F2 to F7. In these tables the maximum possible error which could occur for each parameter is combined to determine an overall estimate of the worst case error for a given time period and environmental media. These results are displayed in Table F.1. The property parameters are combined in two ways, addition and multiplication. The formula used for combining the relative errors for each case are presented below assuming linearly independent variables as discussed in Chapter 7.

For the addition of three parameters (x,y,z) with respective coefficients (a,b,c) to produce F, the error in the result (dF) is given by equation F.2.

$$F = ax+by+cz \quad \textbf{(F.1)}$$

$$dF = \mathrm{sqrt}((adx)^2 + (bdy)^2 + (cdz)^2) \quad \textbf{(F.2)}$$

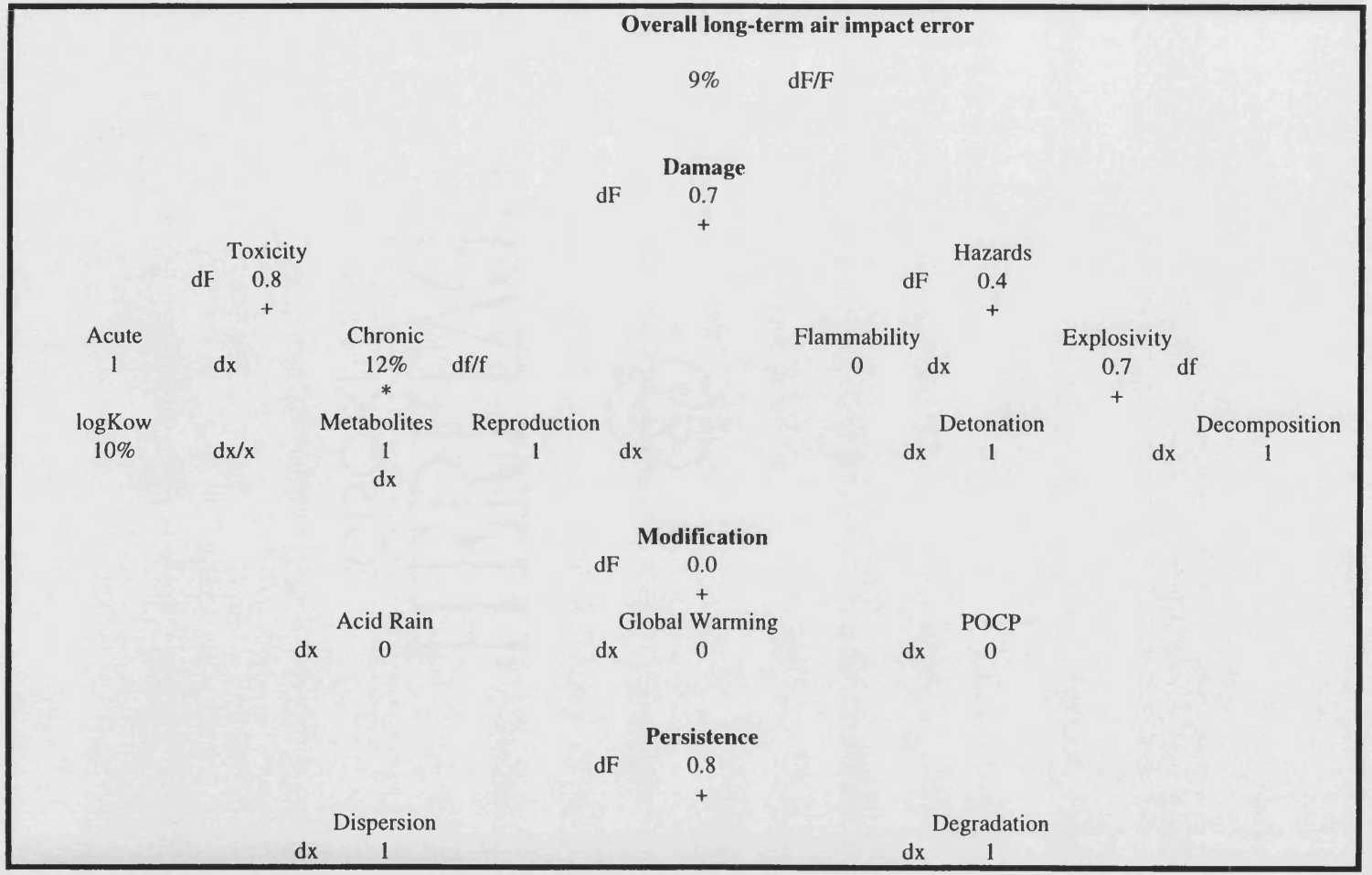
For the multiplication of two parameters (x,y) with respective coefficients (a,c) and indices (b,d) to produce F, the relative error in the results dF/F is given by equation F.4.

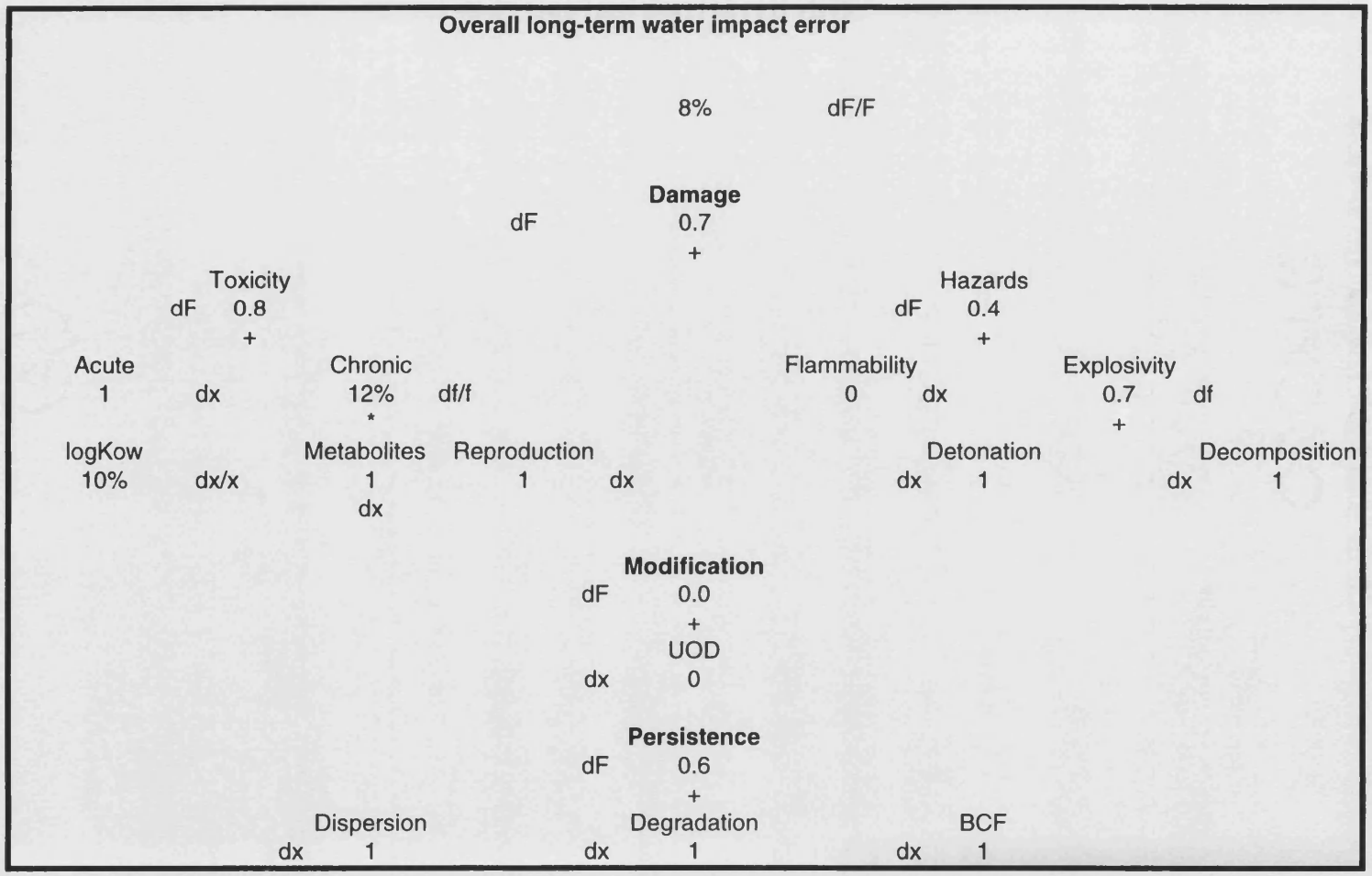
$$F = ax^b * c\,y^d \quad \textbf{(F.3)}$$

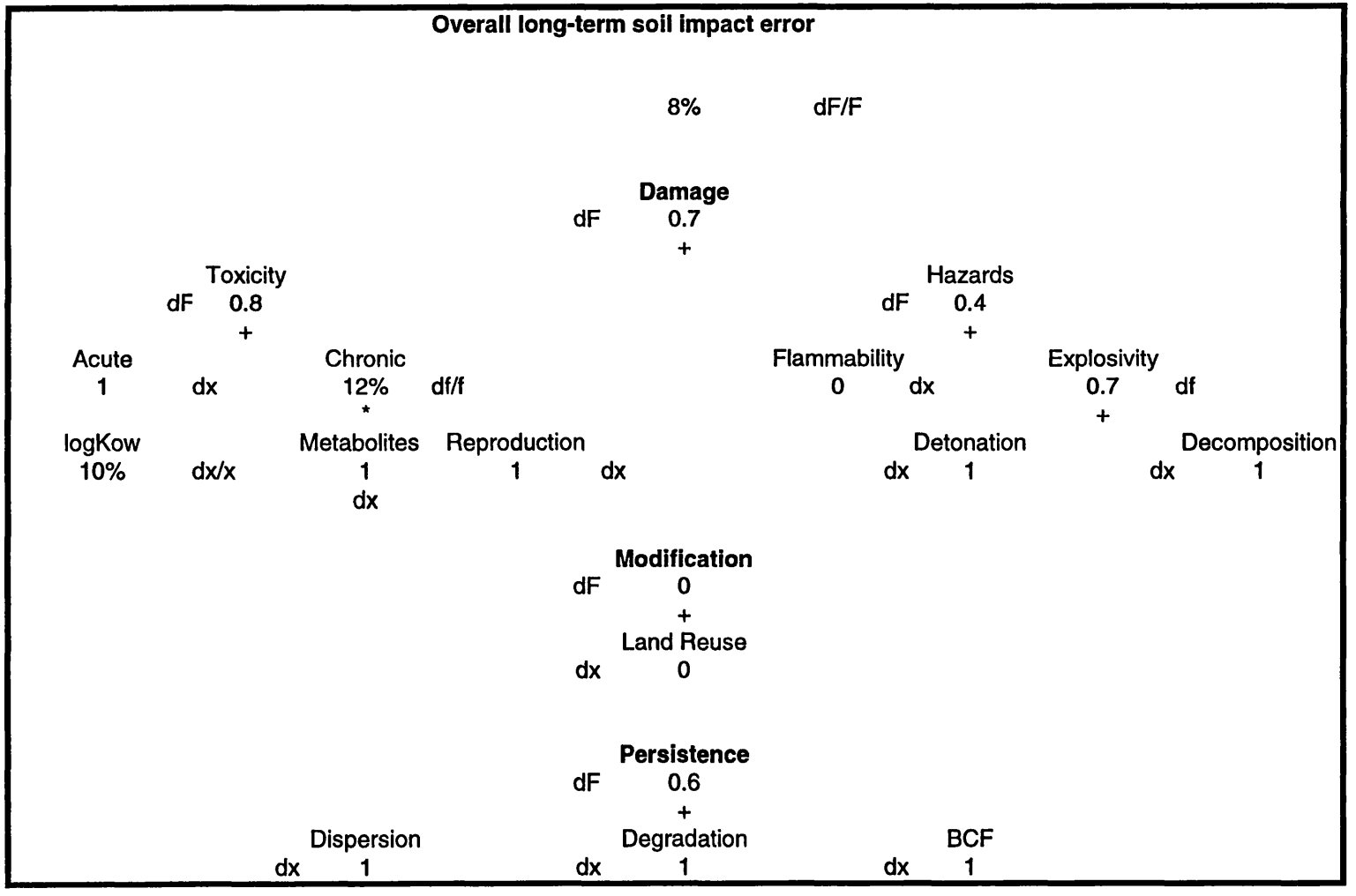
$$dF/F = \mathrm{sqrt}((bdx/x)^2+(ddy/y)^2) \quad \textbf{(F.4)}$$

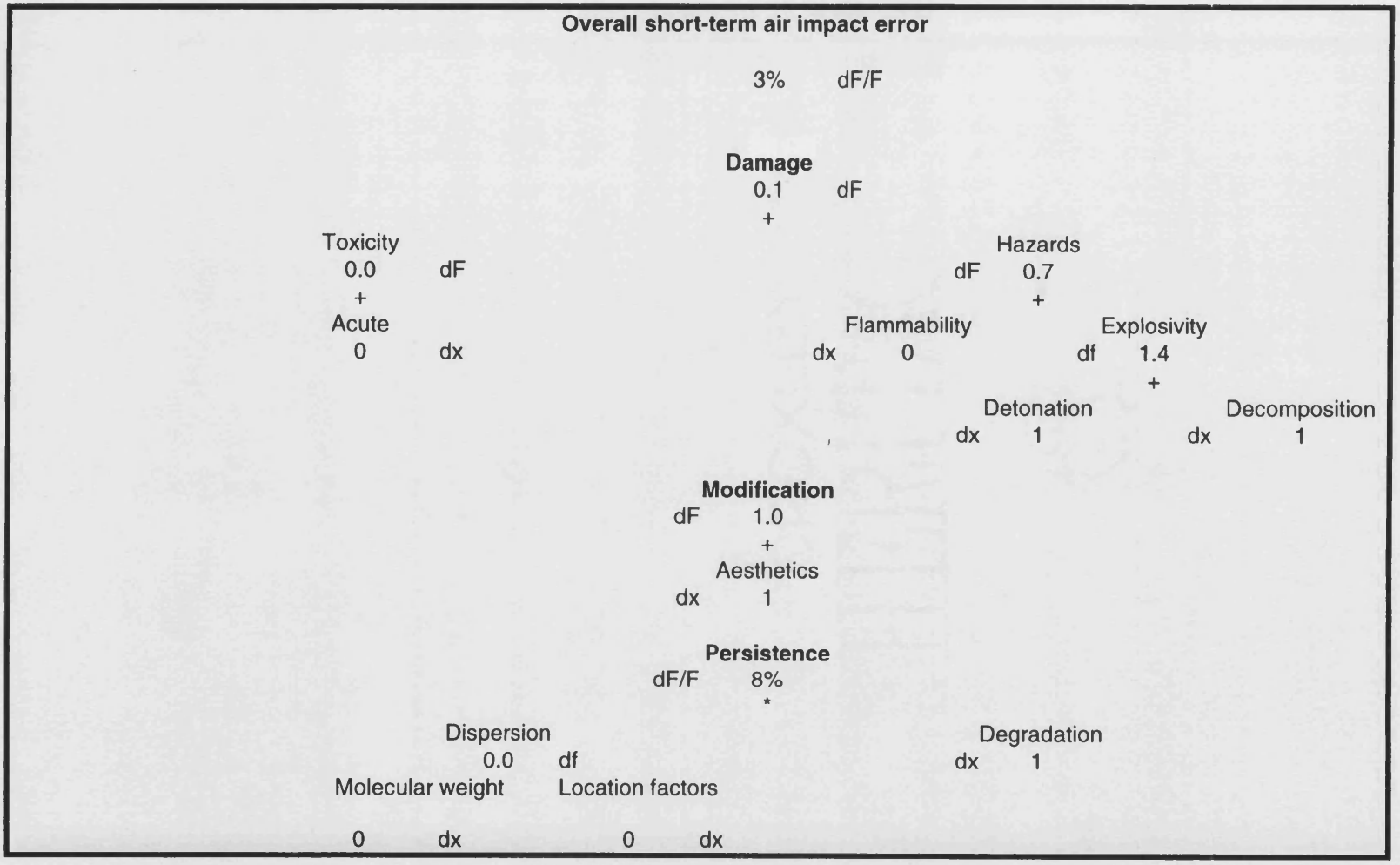
Table F.1 Worst case relative error results for the calculation of impact scores

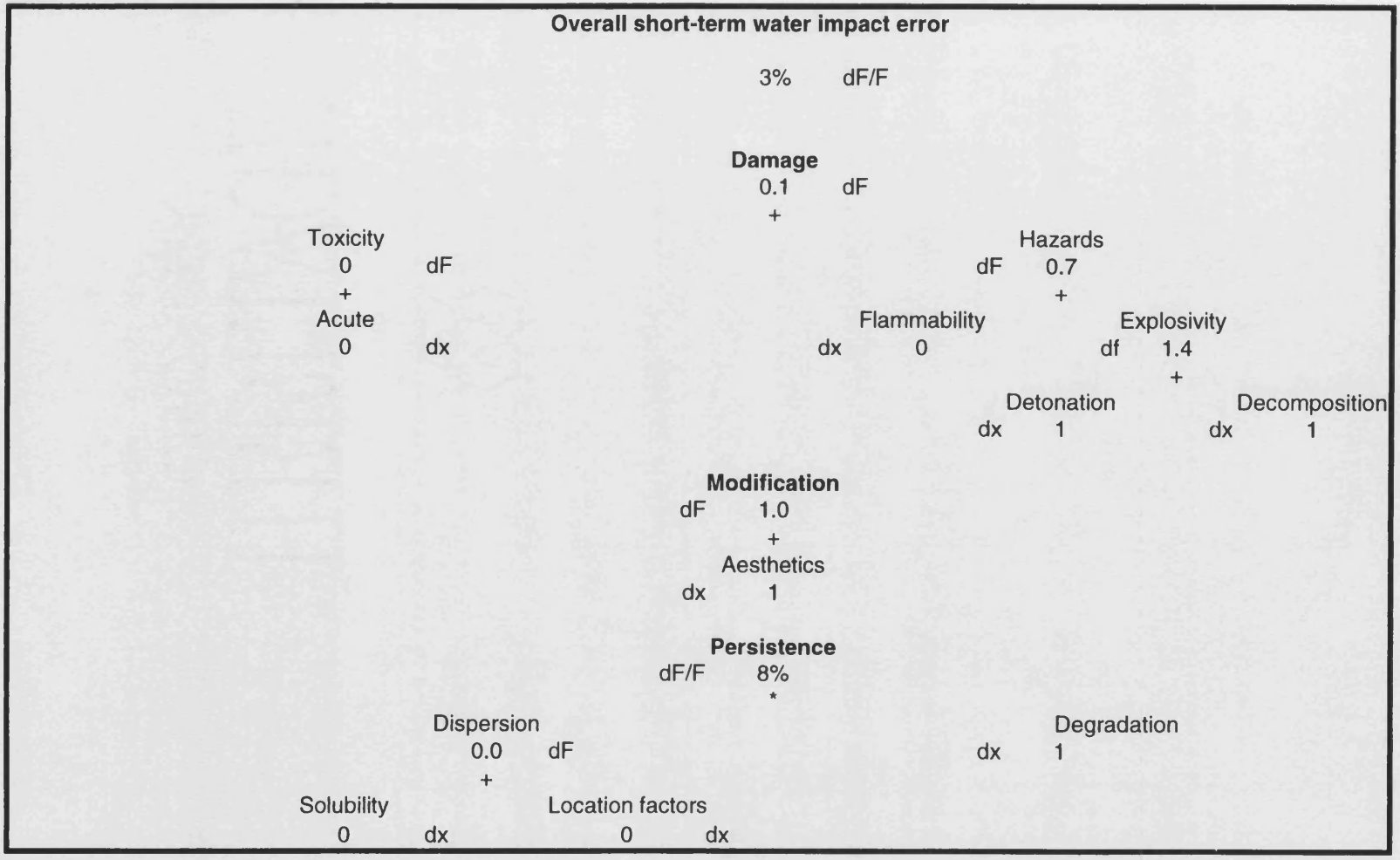
Medium	Long-term dF/F	Short-term dF/F
Air	9%	3%
Water	8%	3%
Soil	8%	3%

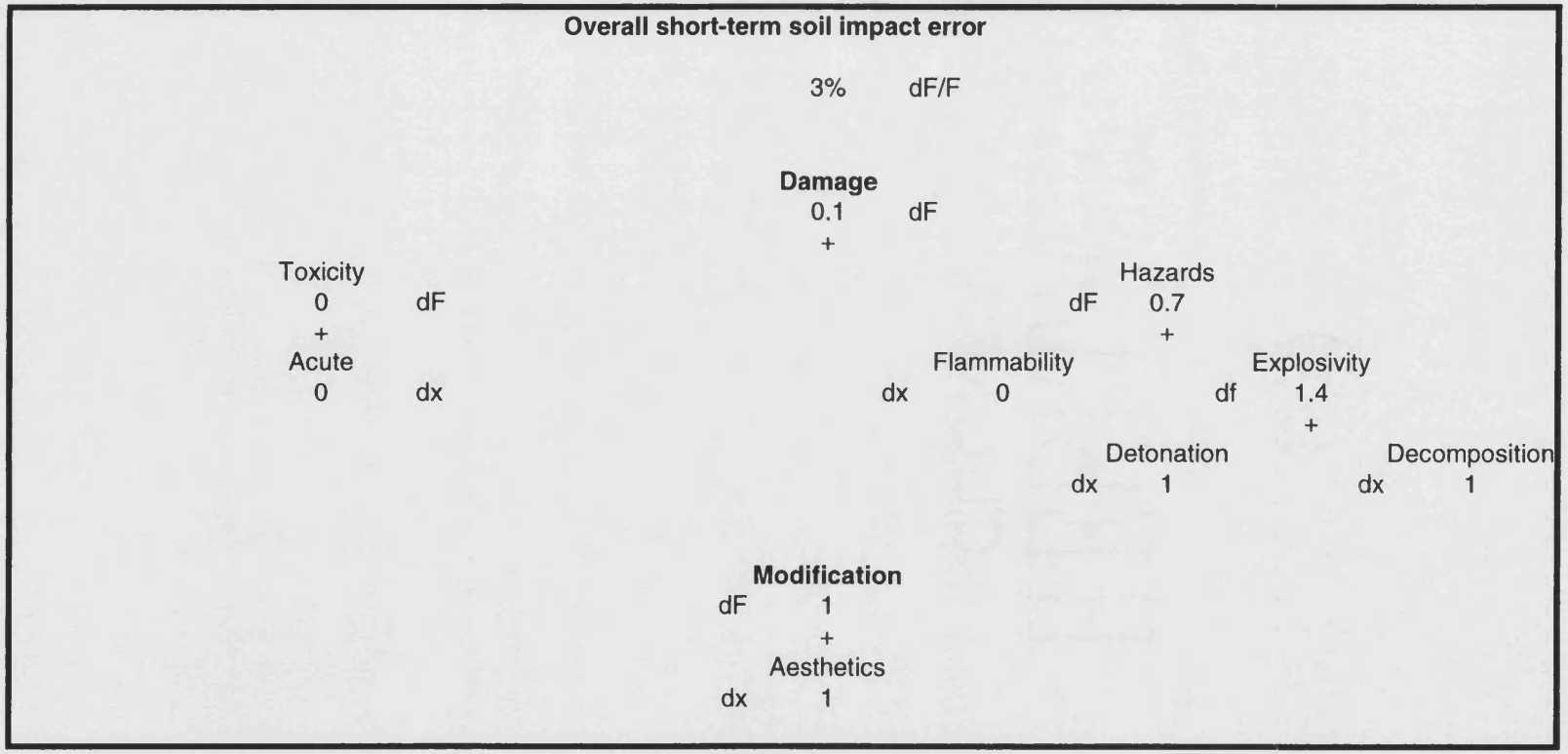

Overall long-term air impact error
9%
dF/F
Damage
dF
0.7
+
Toxicity
dF
0.8
+
Acute
1
dx
Chronic
12%
df/f
*
logKow
10%
dx/x
Metabolites
1
dx
Reproduction
1
dx
Hazards
dF
0.4
+
Flammability
0
dx
Explosivity
0.7
df
+
Detonation
dx
1
Decomposition
dx
1
Modification
dF
0.0
+
Acid Rain
dx
0
Global Warming
dx
0
POCP
dx
0
Persistence
dF
0.8
+
Dispersion
dx
1
Degradation
dx
1


Overall long-term water impact error
8%
dF/F
Damage
dF
0.7
+
Toxicity
dF
0.8
+
Hazards
dF
0.4
+
Acute
1
dx
logKow
10%
dx/x
Chronic
12%
df/f
*
Metabolites
1
dx
Reproduction
1
dx
Flammability
0
dx
Explosivity
0.7
df
+
Detonation
dx
1
Decomposition
dx
1
Modification
dF
0.0
+
UOD
dx
0
Persistence
dF
0.6
+
Dispersion
dx
1
Degradation
dx
1
BCF
dx
1


Overall long-term soil impact error
8%
dF/F
Damage
dF 0.7
+
Toxicity
dF 0.8
+
Acute
1
dx
Chronic
12%
df/f
*
logKow
10%
dx/x
Metabolites
1
dx
Reproduction
1
dx
Hazards
dF 0.4
+
Flammability
0
dx
Explosivity
0.7
df
+
Detonation
dx 1
Decomposition
dx 1
Modification
dF 0
+
Land Reuse
dx 0
Persistence
dF 0.6
+
Dispersion
dx 1
Degradation
dx 1
BCF
dx 1

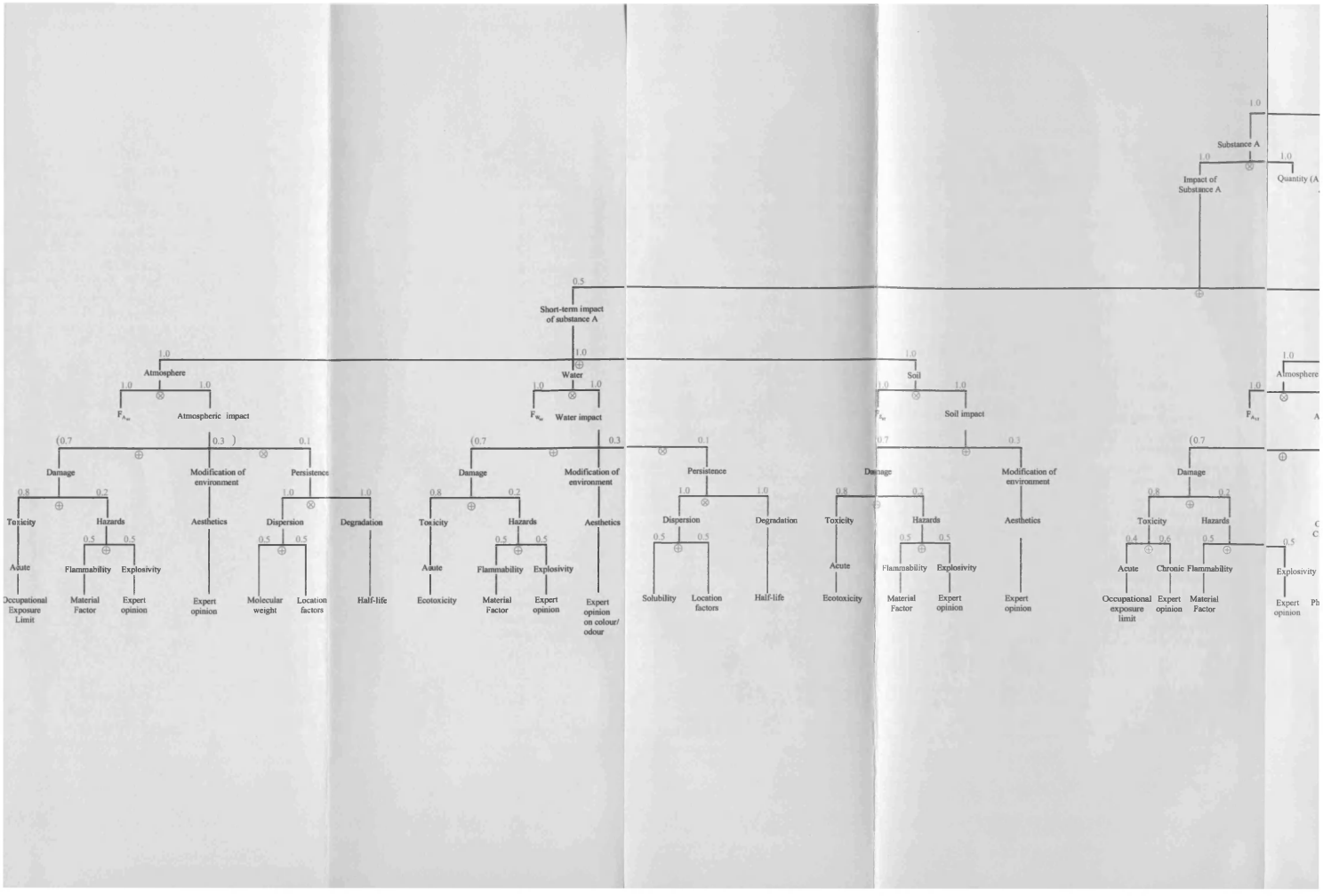

Overall short-term air impact error
3% dF/F
Damage
0.1 dF
+
Toxicity
0.0 dF
+
Acute
0 dx
Hazards
dF 0.7
+
Flammability
dx 0
Explosivity
df 1.4
+
Detonation
dx 1
Decomposition
dx 1
Modification
dF 1.0
+
Aesthetics
dx 1
Persistence
dF/F 8%
*
Dispersion
0.0 df
Molecular weight
0 dx
Location factors
0 dx
Degradation
dx 1

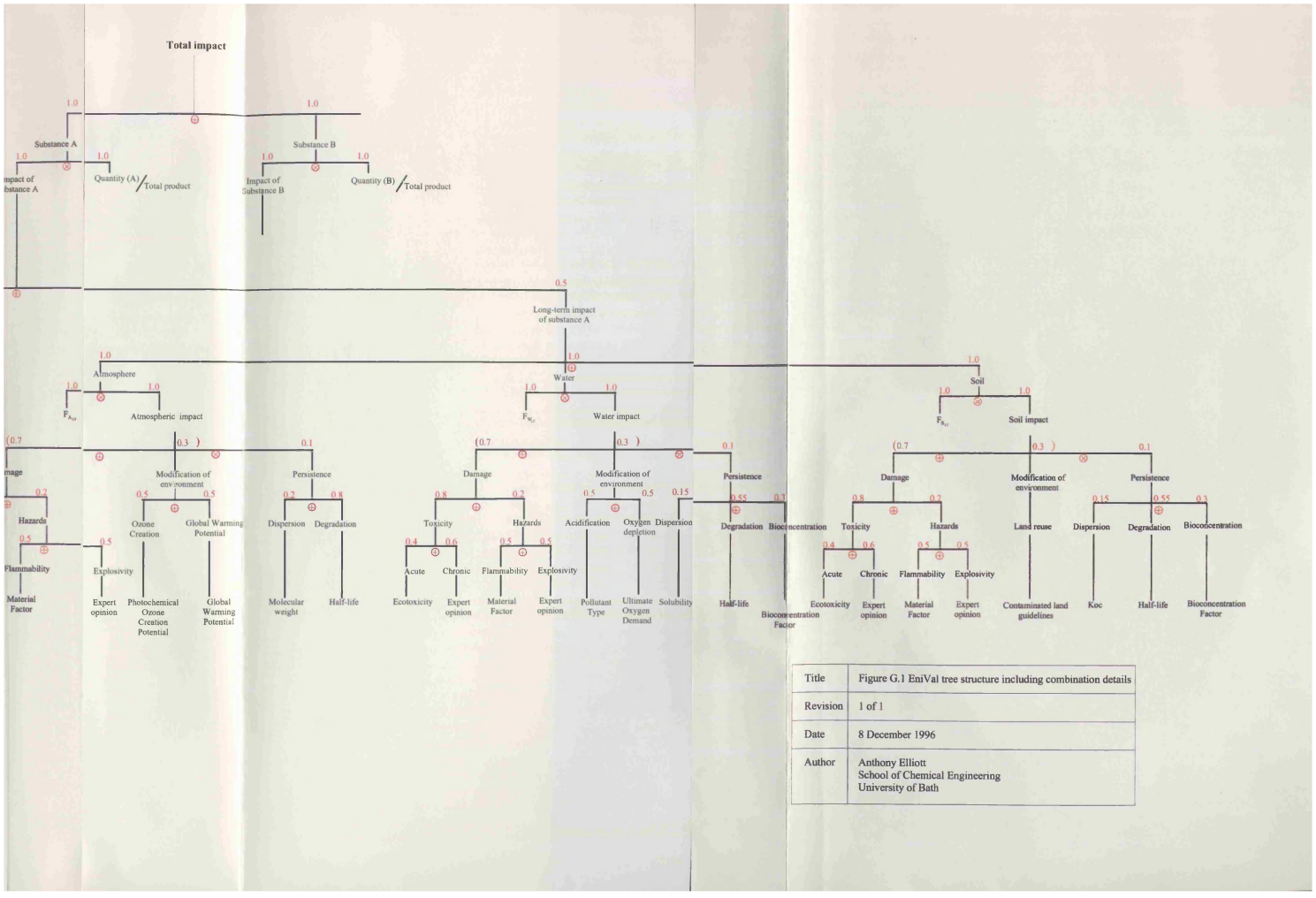

Overall short-term water impact error
3% dF/F
Damage
0.1 dF
+
Toxicity
0 dF
+
Acute
0 dx
Hazards
dF 0.7
+
Flammability
dx 0
Explosivity
df 1.4
+
Detonation
dx 1
Decomposition
dx 1
Modification
dF 1.0
+
Aesthetics
dx 1
Persistence
dF/F 8%
*
Dispersion
0.0 dF
+
Solubility
0 dx
Location factors
0 dx
Degradation
dx 1


Overall short-term soil impact error
3% dF/F
Damage
0.1 dF
+
Toxicity
0 dF
+
Acute
0 dx
Hazards
dF 0.7
+
Flammability
dx 0
Explosivity
df 1.4
+
Detonation
dx 1
Decomposition
dx 1
Modification
dF 1
+
Aesthetics
dx 1

Appendix G

'Lift-out diagram of the tree structure for EniVal'


Substance A
Impact of Substance A
Quantity (A
Short-term impact of substance A
Atmosphere
Atmospheric impact
Water
Water impact
Soil
Soil impact
Damage
Modification of environment
Persistence
Toxicity
Hazards
Aesthetics
Dispersion
Degradation
Acute
Flammability
Explosivity
Occupational Exposure Limit
Material Factor
Expert opinion
Molecular weight
Location factors
Half-life
Ecotoxicity
Solubility
Expert opinion on colour/ odour
Chronic
Occupational exposure limit
Explosivity



Title	Figure G.1 EniVal tree structure including combination details
Revision	1 of 1
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